Appendix E-1

DRAFT *IN-SITU* BIOPILOT REPORT

Ciba-Geigy Site

SUBMITTED BY

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SUBMITTED TO

EPA
United States Environmental Protection Agency

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Ciba Specialty Chemicals
Corporate Remediation
Toms River, New Jersey
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1.0 INTRODUCTION AND BACKGROUND

Ciba Specialty Chemicals Corporation owns a former industrial facility in Toms River, New Jersey. The historical manufacturing operations, wastewater treatment and disposal practices have resulted in the contamination of soil and groundwater. Remedial activities to address the site-related contamination are regulated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The contaminated portion of the former industrial facility is herein referred to as the "Site".

In situ bioremediation is a candidate technology for some contaminated soils, including soils containing NAPL, both above and below the water table. Pertinent background information for this project is contained in the "In-Situ Bioremediation Pilot Study Work Plan" (Ciba 1996d).

1.1 STUDY OBJECTIVES

The pilot system focuses on aerobic metabolism of Site contaminants of concern (COCs) for the purpose of providing sufficient data to evaluate *in-situ* aerobic biological treatment for remediating Site soils. It is important that the pilot study establish the potential rates of removal and the extent to which contaminants are removed from NAPL impacted soil. The pilot system was designed to provide aggressive treatment in order to provide results within the time constraints of the study as well as provide for a mass balance of contaminants. The mass of contaminants removed was determined by completing a mass balance on the pilot cell using initial and final soil concentrations and mass inputs/outputs.

1.2 PROJECT OVERVIEW

The project was divided into several phases representing milestones for pilot study completion.

Phase I - Site Characterization, Design, and Construction

The location selected for the biopilot cell was based on high concentrations of Site COCs. The second criteria was a geology suitable for the installation of a sheet pile wall to isolate a large cube of soil. The Former South Dye Area was selected based on the high contaminant concentrations in the former Building 102 underground storage tank area,

and also the existence of the Cohansey Yellow Clay at a depth of 30 feet from ground surface. The clay was both thick enough for the sheet pile wall to key into and located at an ideal depth for the desired pilot cell size. Construction was completed in the fourth quarter of 1996.

Phase II - Pilot System Start-Up

The system start up period was a relatively short testing of the pumps, piping and oxygen transfer equipment. A leak test was also performed on the cell structure by increasing the saturated thickness several feet and monitoring water levels over several days to quantify any leakage. After 1 week of testing the equipment the system was started for continuous operation.

Phase III - Operations and Performance Evaluation

The system operational period ran from December 1996 through February 1999. Two sets of 125 soil samples each were collected during the operational period, one in May 1998 and the second in January 1999. Groundwater parameters were monitored throughout the 2 year operational period.

Phase IV – Rebound Testing

After the second set of soil samples was collected the system recycle rate was reduced to change the groundwater velocity between the recharge and extraction wells from 10 ft. per day to approximately 1 ft. per day. Oxygenation of the system was terminated and the surface infiltration trenches were not used. This condition was set up to evaluate rebound effects that might occur in the field after an active biological system is shut down. This testing is currently continuing.

2.0 SYSTEM DESIGN, CONSTRUCTION, START UP AND OPERATION

The biopilot cell and associated process control equipment was constructed during the third quarter of 1996, with start up of the process in December 1996. The operational period for the study ran from December 1996 through February 1999. Some testing of rebound effects is continuing.

2.1 OVERVIEW OF BIOPILOT STUDY DESIGN

The basic design of the pilot cell was an *in-situ* soil treatment area, formed by physical isolation of a 1000 cubic yard block of soil. Isolation of the soil and groundwater from outside influence permitted an evaluation of biological degradation within the cell based on contaminant mass balance and measurement of oxygen utilization and formation of degradation products.

2.1.1 Treatment Process Concept

The aerobic biological process within the cell was stimulated by the addition of oxygen and inorganic forms of nitrogen and phosphorous, the absence of which commonly limit bioactivity. Sufficient naturally occurring bacteria were expected to be present that were capable of degrading the contaminants in the cell, especially after significant acclimation time (tens of years) that had transpired between the time of contaminant release to the soil and the time of the biopilot installation.

2.1.2 Design and System Operation Features

This system was designed to maintain an aerobic condition throughout the cell by delivering oxygen to the subsurface by dissolution of high partial pressure (95%) oxygen into the recycled groundwater and by sparging oxygen directly to the subsurface through sparge wells. Volatilization of contaminants from the subsurface was minimized by the use of 95% oxygen, significantly reducing the volume of gas introduced into the system, which in turn reduced the volume of off gas generated. The surface cover on the cell also controlled volatilization and permitted measurement of off gases beneath the cover. Groundwater extraction and recharge were used to distribute oxygen, nutrients, and to some extent contaminants and their degradation products, within the cell. In-line probes

continuously monitored the extraction and recharge groundwater for pH and dissolved oxygen.

2.2 CONSTRUCTION

Construction of the system included the isolation of the soil block with sheet piling, installation of the monitoring components within the cell and assembly of the extraction and recharge piping, oxygenation equipment and external monitoring components. The oxygenation system, control devices, external monitoring devices, and data acquisition system were housed in a trailer unit located next to the cell.

2.2.1 Site Preparation

The site selected for the biopilot cell was located within the former Production Area, specifically the former Building 102 footprint in the Former South Dye Area. The location is indicated in **Figure 2-1**. Although the building was previously demolished, the concrete footings below grade remained. To make the location accessible for sheet piling installation, the top six feet of soil was removed to expose any subsurface concrete structures that remained from Building 102. Three large rectangular footings were removed, and the excavated soil placed back in the top of the cell. The volume taken up by the concrete that was removed was replaced with uncontaminated native fill from the Site. This was completed prior to the installation of the sheet pile walls and cell monitoring devices, and also before any soil characterization sampling was undertaken.

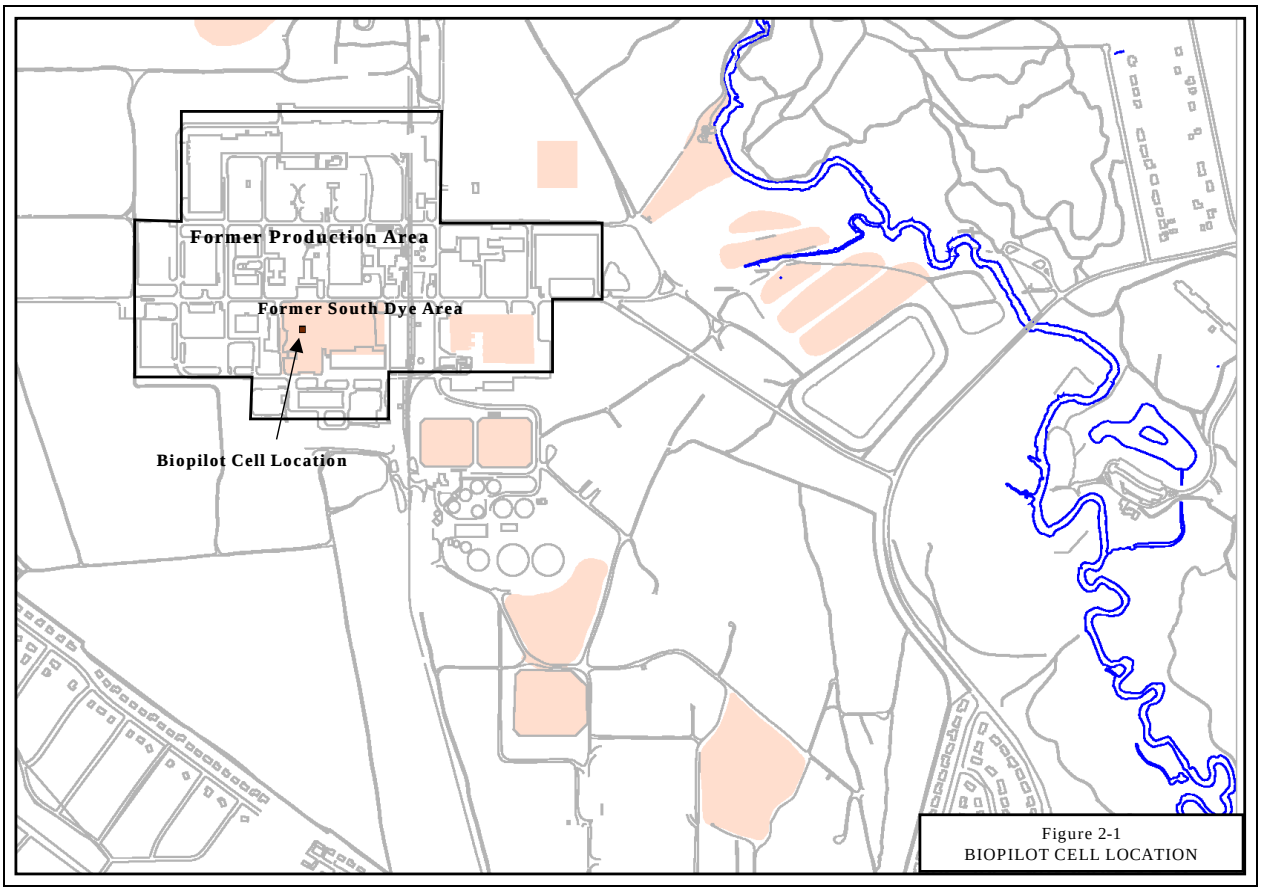


Figure 2-1
BIOPILOT CELL LOCATION

2.2.2 Subsurface Barrier Wall

The pilot cell subsurface barrier walls were constructed using Waterloo interlocking steel sheet piling. A set of sheet pile walls was driven into the Cohansey Yellow Clay approximately 30 feet below ground surface to isolate a cube of soil 30 feet on each side. A vibratory driver was used to install the sheet piling in approximately 5 foot lifts after the walls were interlocked into a box structure above ground. The interlocking joints were grouted with a bentonite slurry through the full depth of the walls after installation was completed to assure the hydraulic integrity of the cell.

2.2.3 Surface Cover

The surface of the cell was covered with a geotextile encased bentonite composite liner that was installed six inches below final grade and covered with clean soil. Bentonite was also layered around the edges of the liner where it met the corrugated sheet pile wall and where monitoring devices protruded to effect a complete seal. Three vents were installed beneath the surface liner to permit monitoring of escaping gases. A sprung structure

covered the entire cell in order to reduce drying of the surface seal and prevent precipitation from entering the cell.

2.2.4 Groundwater Recirculation Wells

Six wells were installed for the purpose of groundwater extraction and recharge. Three wells spaced evenly along the north side of the cell five feet inside of the sheet pile wall were configured for groundwater extraction. The other three wells were installed in the same manner on the south side of the cell and configured for groundwater recharge. All six wells were constructed of 4 inch ID stainless steel with 10 foot screened intervals that terminated at the surface of the Yellow Clay at the bottom of the cell. The well screens were wrapped welded wire type 304 stainless steel with a slot size of 0.020-inch. Variable speed pollution recovery grade submersible pumps were installed to provide a target extraction rate of five GPM from each of the three extraction wells.

The groundwater wells installed in the biopilot were not developed by conventional methods after installation because movement of fine materials and contaminants within the cell by aggressive well development would have been greatly exaggerated compared to full scale installation of an *in-situ* biological system. When the extraction wells were started for the first time the return flow was directed to the surface trenches to avoid plugging the recharge well screens with fine materials. This flow diversion continued for several minutes until the extracted groundwater became clear of fines.

2.2.5 Surface Infiltration Trenches

Two surface infiltration trenches were constructed to deliver approximately half of the recharge water to the unsaturated zone. These were constructed of two foot deep concrete walls spaced 1.5 feet apart, and ran the length of the cell ten feet inside of the north and south sheet pile walls as shown in **Figure 2-2.** A perforated pipe installed over the length of the infiltration trench distributed the recharge flow across the entire surface area inside of the trench walls. The flow to the trenches was sufficient to maintain standing water across the length of the trench and distribute recharge water to the unsaturated zone as uniformly as possible. Plastic sheeting was used to form a floating cover over the standing liquid in the trenches to minimize volatile losses. The top 8 to 12 inches of the trench

surfaces were tilled once after 14 months of operation in to alleviate minor plugging that had occurred over time.

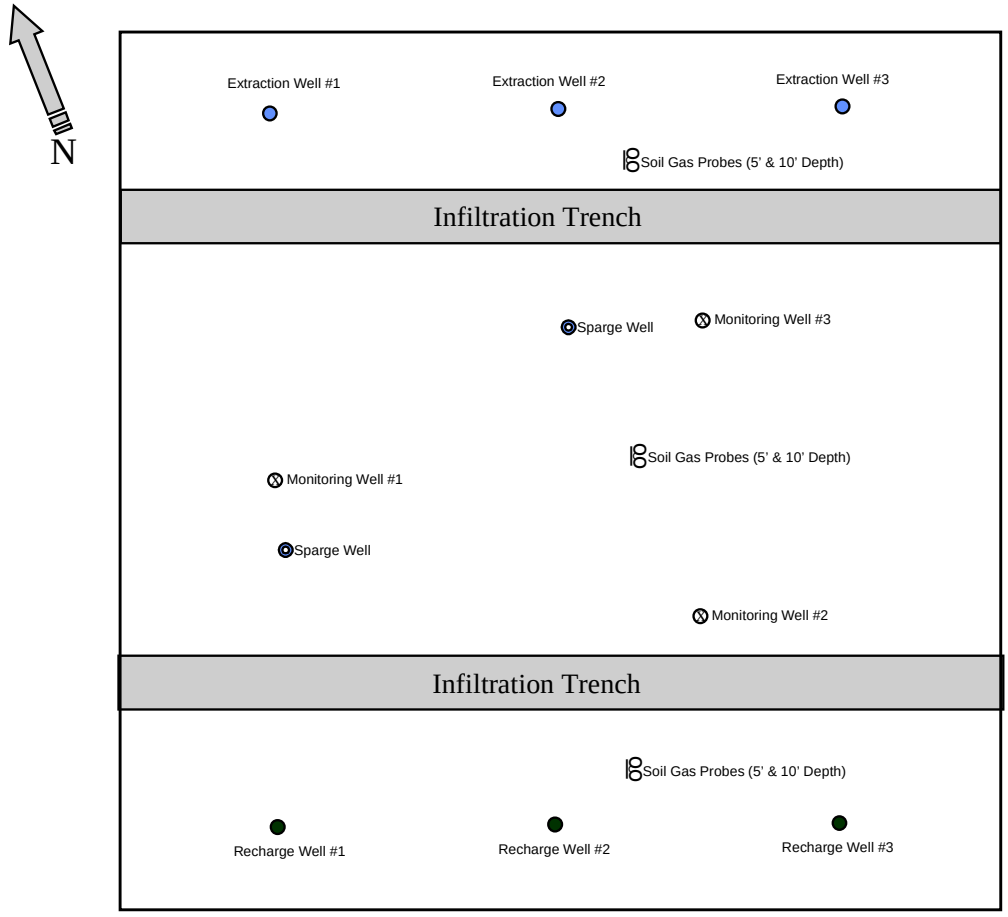


Figure 2-2
Plan View of Wells and Monitoring Components

Figure 2-3 is a section view of the biopilot cell indicating the groundwater extraction and recharge distribution, along with the oxygen distribution points.

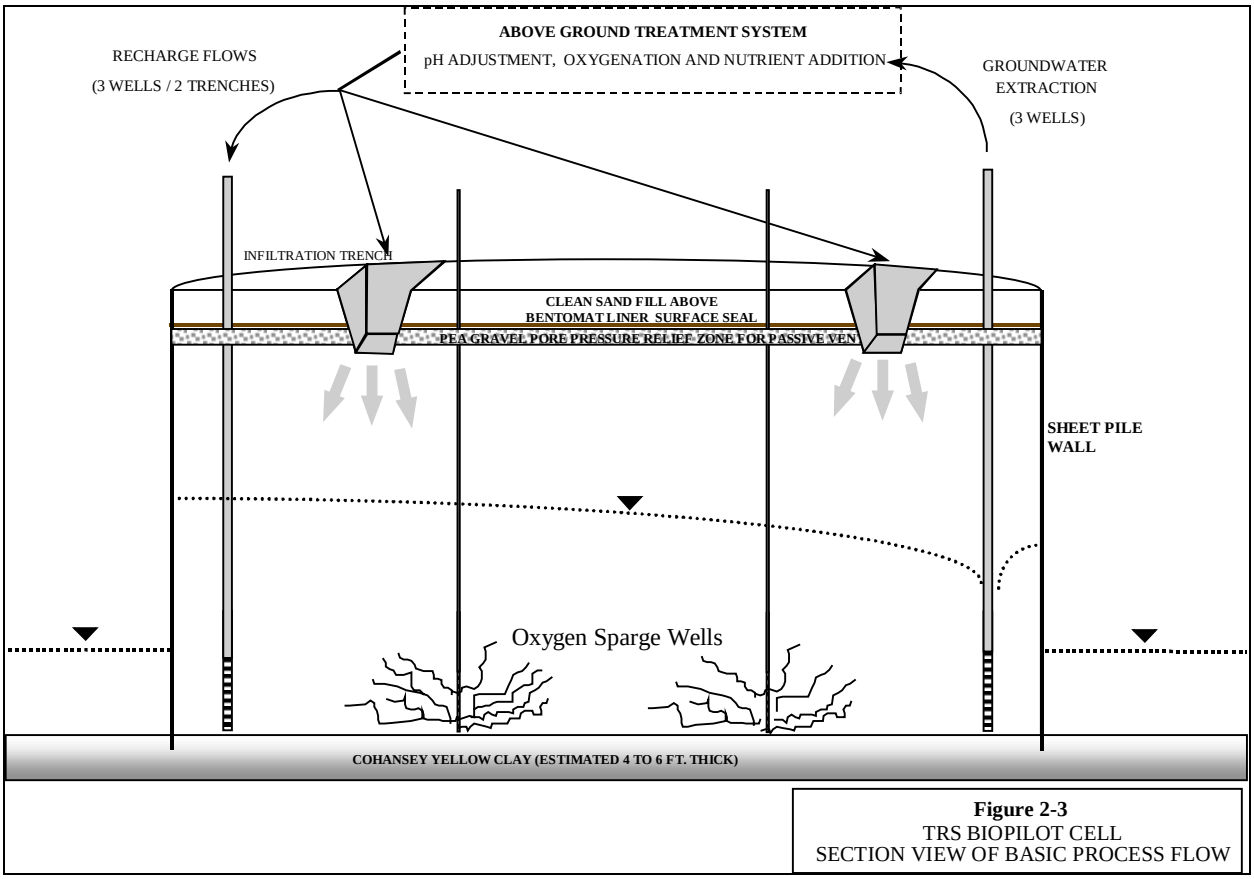


Figure 2-3
TRS BIOPILOT CELL
SECTION VIEW OF BASIC PROCESS FLOW

2.2.6 Oxygen Delivery Equipment

In order to limit volatilization of contaminants as much as possible, high partial pressure oxygen (> 95%) was generated on site for oxygenation purposes. This significantly reduced the volume of gas injected into the cell required to provide sufficient oxygenation to maintain aerobic conditions. The oxygen was generated at the cell location using compressed air and a pressure swing adsorption unit, and was stored in a tank outside of the trailer unit. The system was capable of generating 25 SCFH of 95% oxygen.

Oxygen was sparged to the subsurface through 2 sparge wells that were each screened over a 6 inch interval at the bottom of the cell, just above the clay. An automatic timer system cycled alternating pulses of oxygen to the wells.

A downflow bubble contactor in the groundwater recycle line introduced oxygen directly into the groundwater.

2.2.7 Monitoring Devices

Unsaturated zone monitoring components consisted of three nested pairs of soil gas probes and three nested pairs of lysimeters. All pairs consisted of sample depths of 5 and 10 feet below ground surface. The layout of the biopilot cell devices are indicated in plan and section view in **Figures 2-2 and 2-3.**

2.3 START UP AND OPERATION

2.3.1 Start Up Procedure

Groundwater extraction was started at 5 GPM for each of the three extraction wells using variable speed drive controllers. Because there was significant drawdown at the 5 GPM flow rates and some cavitation eventually occurred, the flow rates for each well were reduced to 4 GPM for the study duration. Whenever the extraction wells were started the recharge flow was directed to the trenches only until the fine materials were flushed from the system. This flushing of fines took from 3 to 5 minutes. Once clear water was being extracted and all the air was purged from the piping the recharge flow was adjusted by manual valves to distribute 2 GPM to each recharge well and 3 GPM to each infiltration trench. After the flows were set the oxygenation system was started. The downflow contactor received 0.2 liters per minute (LPM) high partial pressure oxygen, which was regulated with a manually adjusted flow meter. The sparge wells were automated, requiring no operator adjustment.

2.1.3.1 Daily Operation

Daily operation of the pilot required minimal operator intervention. The groundwater pumping system proved reliable, and the automated oxygenation through the sparge wells operated on a consistent basis. The system was checked on a daily basis for groundwater extraction and recharge rates and the distribution of the recharge groundwater among the recharge wells and infiltration trenches. The manual valves that controlled the recharge distribution required infrequent adjustment.

2.1.3.2 Groundwater Extraction and Recharge Rates

A groundwater extraction and recharge rate of 12 GPM was maintained with minimal fluctuation through the course of the study. This is slightly lower than the design rate of 15 GPM that was reported in the biopilot work plan because there were limitations on the extraction well recovery rates, and aggressive development of the wells was avoided to

prevent excessive cell disturbances that would be exaggerated on the pilot-scale compared to a full-scale installation.

2.1.3.3 Oxygen Delivery

A programmable timer was used to energize solenoid valves to send oxygen to the sparge wells at 4 hour intervals, alternating between the two wells. Each well was sparged three times daily with 12.5 cubic feet of oxygen delivered during each sparge interval. The sparge pulse was delivered over a five minute interval at a 2.5 cubic foot per minute rate.

The groundwater downflow bubble contactor dissolved 0.2 liters per minute of oxygen into the recycled groundwater. The gas flow rate was controlled by a manually adjusted flowmeter. The rate of oxygen delivery was balanced with the groundwater flow so that there was no carryover of gas escaping from the bottom of the contactor, and all the gas went into solution. The downflow contactor was constructed of reinforced glass, allowing for visual inspection of the bubble behavior inside and verification that gas was not escaping out of the bottom.

The combination of the direct oxygen sparging and the contactor dissolution of oxygen into the recycled groundwater delivered approximately 3.6 pounds of oxygen per day into the biopilot cell, as reported in Table 2-1.

TABLE 2-1
Oxygen Delivery Rate

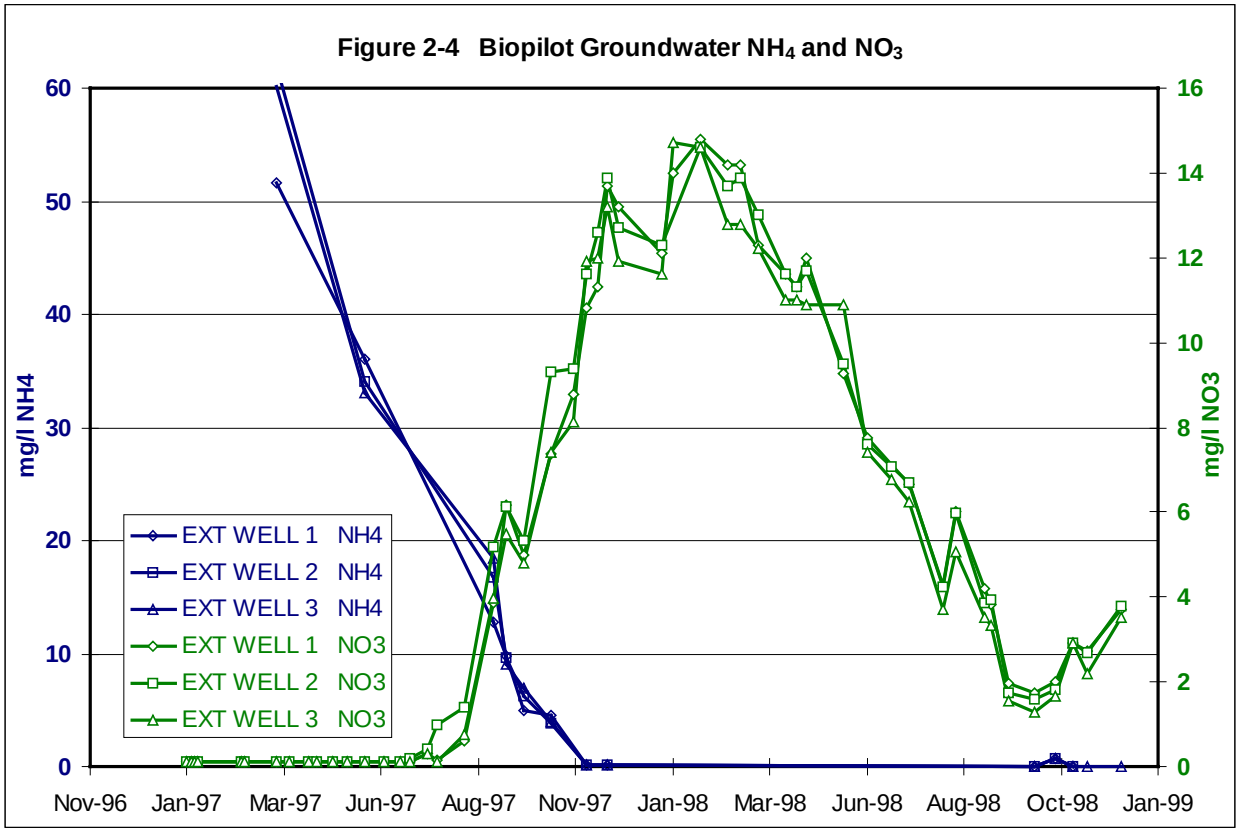
(Using 95% oxygen)	ml/min	liters/day	lbs/day
Contactor	200	288	0.43
Sparging		2100	3.14
Total		2388	3.57

Attempts were not made to quantify the transfer efficiency of the directly sparged oxygen, but because the pulse volumes were small and spaced several hours apart, it is assumed that significant channeling and short circuiting to the surface and/or nearby wells did not occur.

2.1.3.4 Nutrient Delivery and pH Adjustment

Nitrogen was added to the system early in the study as an aqueous ammonia solution. An excess was added based on the theoretical oxygen demand calculated for the contaminant

mass estimated to reside within the cell. The ammonium concentration was monitored throughout the course of the study, as well as the nitrate levels that increased after nitrification became significant. The ammonia and nitrate concentrations are presented in Figure 2-4. Ammonia was added to the system a second time after 650 days of operation because the nitrate concentration continued to decline. Nitrification of this ammonia was evident upon its addition to the system.



Even after adding significant amounts of phosphorous in the form of phosphoric acid solution, the detection of residual phosphate in the recycled groundwater was infrequent. It was assumed that, although the phosphate precipitated within the system, sufficient amounts were still available to avoid nutrient limitation.

The groundwater pH ranged from 6.3 to 6.8 throughout the course of the study, without any chemical additions for adjustment. A significant amount of concrete rubble in the upper soils may have provided buffering capacity and maintained an acceptable pH range. A stripper was installed for a short period of the study to remove CO2 from the soil gas, but its use was discontinued after problems with the passive venting system prevented its effective operation.

2.1.3.5 Maintenance

The cell operated in a satisfactory manner for 24 months, with no significant unanticipated problems. The three injection wells did not develop resistance to flow, as measured by pressure at the well heads. Throughout the operational period the recycled groundwater was distributed evenly among the 5 recharge points within the cell (3 injection wells and 2 infiltration trenches). The three extraction wells were each serviced once during the operational period to remove fine materials from the impellers and check for wear.

3.0 SOIL SAMPLING AND CHARACTERIZATION

Sampling of soil within the cell was used to determine the effects of the biological system on the contaminants by performing a mass balance of the contaminant mass before and after a period of active treatment.

3.1 SAMPLING METHODOLOGY

The soil characterization consisted of the collection and analysis of 125 samples located on the 5 foot grid spacing indicated on Figure 3-1. A two inch diameter vibratory coring device was used to collect continuous samples from the ground surface to the top of the Yellow Clay at each of the 25 locations. Six-foot vertical composite samples were collected at each boring location, representing 0 to 6, 6 to 12, 12 to 18, 18 to 24, and 24 to approximately 30 feet depth intervals from the ground surface. The soil cores were cooled to $4^{O}C$ prior to extruding the soil to minimize volatile losses during handling. A representative amount of soil collected over each 6 foot vertical interval at each sample location on the grid was deposited directly into a specially prepared jar containing methanol. The sample jars with methanol were also cooled to $4^{O}C$ prior to composite sample preparation.

Because the sample grid was measured inward from the sheet pile wall with the soil borings placed on 5 foot centers, the soil blocks represented by an analytical sample were not all the same size. The variation in size can be seen in Figure 3-1, where the corner blocks are the largest, and the remaining perimeter blocks are larger than the interior blocks.

3.2 GEOLOGY

The geology within the biopilot cell was typical of the Site conceptual model for the geology from the ground surface to the depth of the Yellow Clay in the Former South Dye Area. The top 4 to 6 feet consisted of reworked fill material. This was a black sandy fill mixed with small pieces of brick and concrete rubble. There was a consistent layer of mixed coarse to fine poorly sorted sands that extended from 6 to 14 feet below ground surface. From 14 to about 22 feet below ground surface the sands were coarser grained and became saturated. This is typical of the Upper Cohansey Sand Member. The sand graded to finer material with some silty sand stringers beginning at a depth of 25 feet below grade. Fine sands, silts and clay stringers alternated in layers as small as one inch thick from 27 feet to the surface of the clay (Cohansey Yellow Clay Member) at 30 feet. Figure 3-2 presents the Former South Dye area geology in a cross section at the biopilot location.

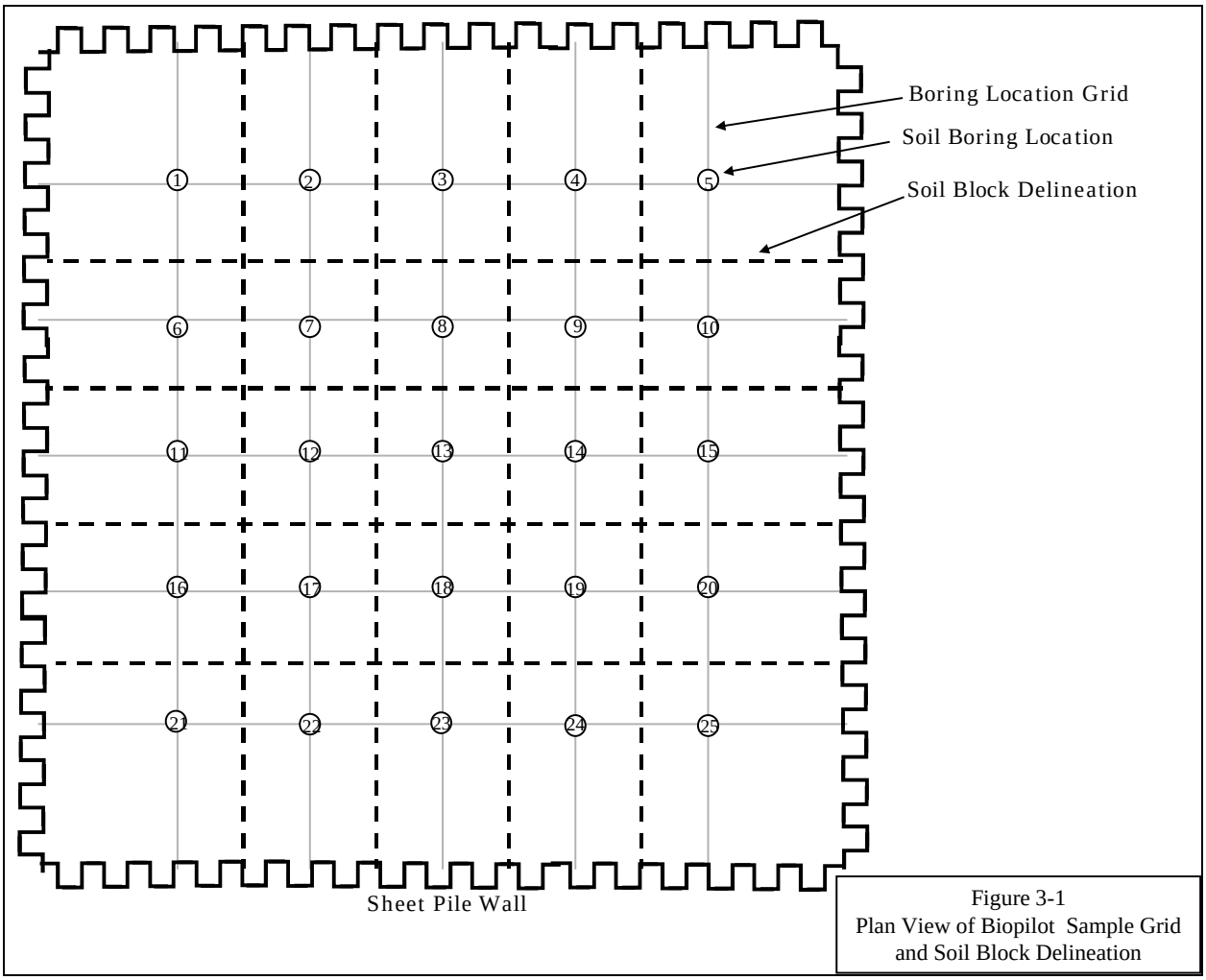
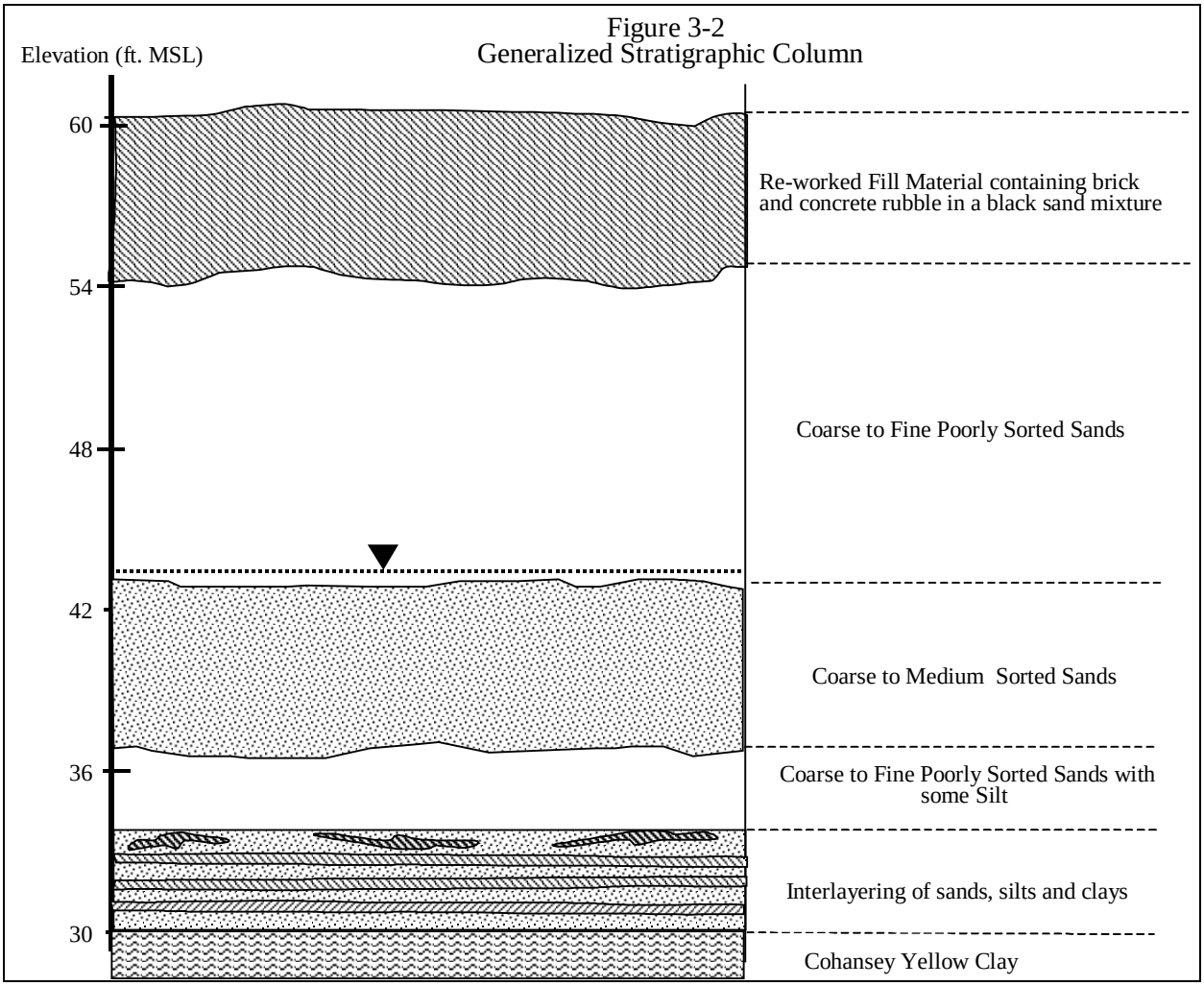


Figure 3-1
Plan View of Biopilot Sample Grid
and Soil Block Delineation

Figure 3-2
Generalized Stratigraphic Column



3.3 ANALYTICAL RESULTS FROM INITIAL SOIL SAMPLES

Table 3.1 is a compilation of the initial contaminant mass estimates within the cell based on the concentrations of contaminants measured in the soil during the initial characterization sample event. The initial organic total target analyte mass estimate was 673 lbs, 97% of which is accounted for by chlorotoluene, dichlorobenzene, and trichlorobenzene isomers.

Table 3.1

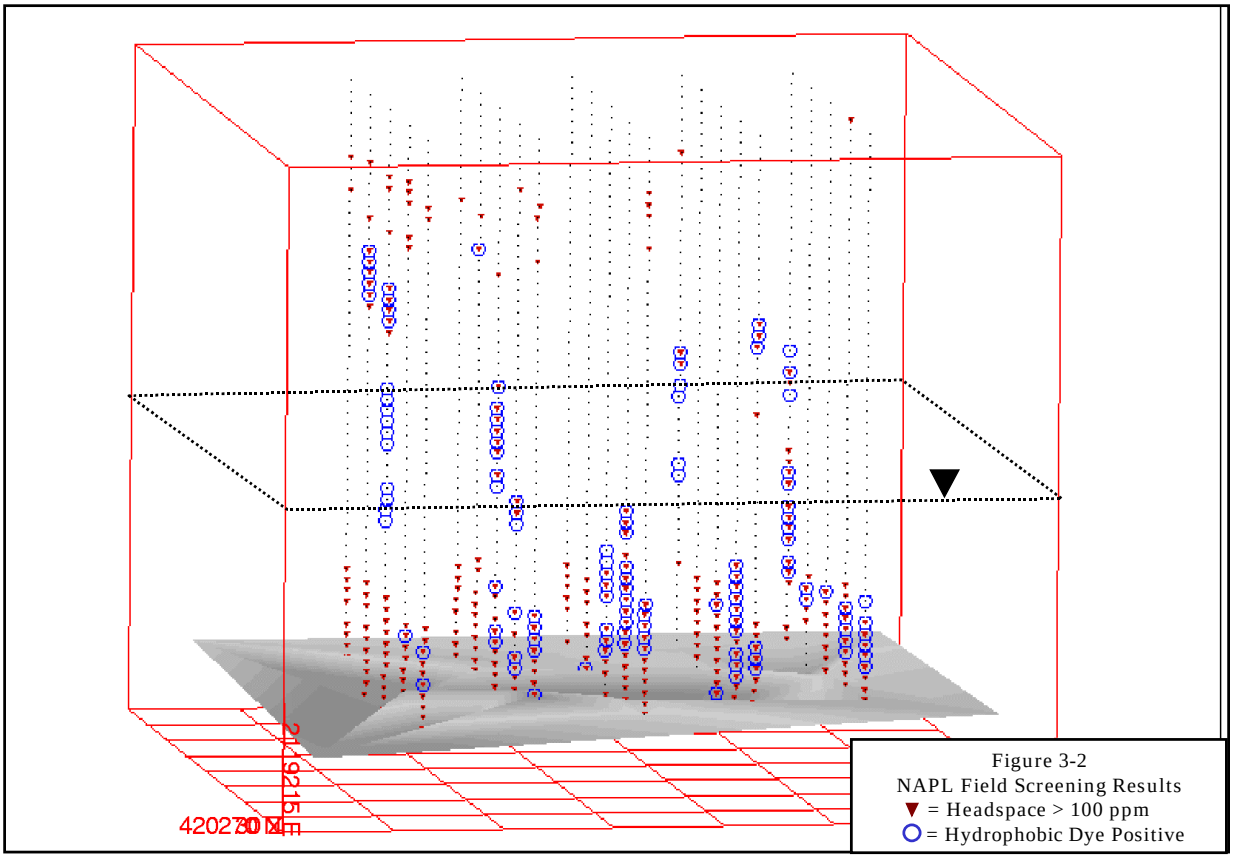
Ciba TRS Biopilot Revised Initial Soil Characterization

Analyte	Estimated Kg	Estimated LBS	Analyte Specific Gravity	% of total
1,2,4-Trichlorobenzene	132.5	291.5	1.463	43.3
1,2-Dichlorobenzene	83.0	182.7	1.288	27.1
2-Chlorotoluene	53.9	118.5	1.076	17.6
1,4-Dichlorobenzene	17.1	37.7	1.288	5.61
Acetone	8.1	17.8	0.788	2.65
1,2,3-Trichlorobenzene	4.4	9.8	1.463	1.46
4-chlorotoluene	2.7	5.9	1.070	0.89
1,3-Dichlorobenzene	2.5	5.6	1.288	0.83
Chlorobenzene	0.64	1.42	1.107	0.21
Naphthalene	0.50	1.10	1.162	0.16
2-Chloronaphthalene	0.29	0.65	1.193	0.10
1,1,2,2-Tetrachloroethane	0.061	0.13	1.586	0.02
TOTAL	**306**	673		**100.0**

Notes: 1.) 3,008,349 lbs of soil based on 1.85 g/cc bulk density;

2.) 224 mg/kg mean soil total target analyte concentration.

NAPL field screening was performed in addition to the 125 composite analytical samples that were used for soil characterization. Headspace measurements of soil placed in sample jars and permitted to equilibrate were used in conjunction with hydrophobic dye screening for NAPL. These methods of field screening have been described in detail in the Fianl NAPL Action Plan Investigation Report (Ciba 1998a). The field screening on the much finer vertical spacing than the soil analytical composites (6 inches instead of 6 feet) could be used to refine the concept of the contaminant distribution within the cell. **Figure 3-2** presents the results of the field screening, indicating where headspace measurements exceeded 100 ppm and hydrophobic dye results were positive for the presence of NAPL.



The field screening data correlate well with the analytical data collected over a much larger vertical spacing, but also indicate more clearly the vertical distribution of the heavily contaminated soil. Most of the contamination in the Former South Dye Area where the pilot cell was constructed has migrated into the silty sands that reside above the Yellow Clay.

Two subsequent sets of soil data were collected from the biopilot cell during the 2 year operational period, one in May of 1998 and the final set in January of 1999. The soil data from all three sample events conducted during the course of the study is attached in electronic format. The performance evaluation for the biological system is based on comparisons made between the initial soil mass and mass remaining after an active treatment period and is discussed in Section 4.0.

4.0 RESULTS AND DISCUSSION

The data trends in this report include operational data from start up through 25 months of active biological treatment, followed by an additional 5 months of monitoring rebound

effects. A tracer study was also conducted to assess the groundwater flow distribution within the cell. The tracer study protocols and results are included in Section 6.0.

Monitoring during the course of the study focused on two issues:

- Operational monitoring of parameters related to the biotic environment, and
- Performance monitoring of groundwater and soil parameters that provided data sufficient to develop rates and extents of contaminant degradation.

In-line probes and a data logging system measured dissolved oxygen and pH of both the extraction and recharge water. Oxygen uptake rates were measured by performing a respiration test on the entire cell by shutting off the subsurface sparging and monitoring O_2 depletion in the extracted groundwater. The extracted groundwater was also monitored for target analytes, chloride ion, dissolved carbon dioxide, alkalinity, and nutrient residuals.

System performance was evaluated by completing a mass balance of the initial contaminant mass and the mass remaining after the treatment period(s). The comparison of before and after treatment utilized 125 initial soil samples and 250 soil samples taken after treatment from similar discrete locations. This evaluation reflected direct losses of contaminant mass. Oxygen uptake, increase in groundwater chloride ion concentration and changes in groundwater contaminant concentrations were also used as indirect indicators of system performance.

A mass balance was also performed using chloride data with respect to accumulation and its relation to degradation of chlorinated organics within the treatment cell. Chloride ion release provides definitive evidence of biodegradation.

4.1 GROUNDWATER PARAMETERS

Groundwater was sampled on a weekly basis from the three extraction wells for the duration of the study. Analytical parameters for these weekly samples included organic target analytes, chloride ion, dissolved oxygen and dissolved carbon dioxide, and alkalinity. Groundwater elevation was also monitored within the cell.

The groundwater elevations were measured in the monitoring wells weekly to allow for mass calculations based on the concentrations of analytes and the volume of water in the cell. The saturated thickness was maintained at approximately 15 feet, or half of the cell depth, throughout the course of the study.

4.1.1 Organic Target Analytes

EPA Method 8260 was used for groundwater analysis, which quantified all the organic COCs in the cell with the exception of nitrobenzene. **Table 4.1** indicates the groundwater concentrations of the target analytes at the start of the operational period in December 1996 and after 24 months of active treatment.

Table 4-1 Volatile Organics in Biopilot Groundwater

Analyte	Initial (ug/l)	720 Days (ug/l)
1,1,1-Trichloroethane	67	19
Benzene	41	1
Trichloroethene	82	27
Chlorobenzene	419	13
1,1,2,2-Tetrachloroethane	304	180
2-Chlorotoluene	9339	162
4-Chlorotoluene	396	11
1,3-Dichlorobenzene	479	12
1,4-Dichlorobenzene	1749	54
1,2-Dichlorobenzene	10824	193
1,2,4-Trichlorobenzene	9504	575
1,2,3-Trichlorobenzene	343	19
Naphthalene	63	8
TVOS	**33,501**	**1,254**

Table 4-2 Semi Volatile Organics in Biopilot Groundwater

Method 8270 Analyte	Initial (ug/l)	After 720 Days
Nitrobenzene	130	< 0.5
Phenol	78	1

N-nitrosodimethylamine	42	28
Benzoic acid	23	< 5
4-Chloro-3-methylphenol	20	< 0.5
2,4-Dichlorophenol	14	< 0.6
2,4,6-Trichlorophenol	14	< 0.5
2,4,5-Trichlorophenol	7	< 0.6
2-Chloronaphthalene	7	< 0.7
Bis(2-chloroethyl)ether	6	< 0.7

Figure 4-1 illustrates the decrease in the groundwater total VOC concentrations measured in the three extraction wells. Extraction wells 1 and 2 exhibited lower concentrations than extraction well 3 over the course of the study. The greater than 1 mg/l organic concentration that was consistent in extraction well 3 was due to 1,2,4-trichlorobenzene, and is assumed to result from the heterogeneity of contaminant distribution in the soil. **Figure 4-2** indicates a similar decreasing trend, focusing on the three contaminants that comprised 97% of the initial soil contaminant mass within the cell. Groundwater measurements taken five feet outside of the sheet pile wall in July and August of 1998 indicated dissolved VOC concentration in excess of 30 mg/l, comparable to the groundwater within the treatment cell at the time of start up.

Figures 4-3, 4-4 and 4-5 provide a mole fraction analysis of data from the individual extraction wells for the three constituents represented in **Figure 4-2**. There were a total of 14 target analytes quantified and tracked in the groundwater within the treatment cell. The mole fraction calculations for the three contaminants represented in the figures include all 14 contaminants that are quantified in the recycle groundwater. Several of the minor target analytes were reduced to levels below detection limits during the course of the study. When an analyte included in the mole fraction calculation was no longer detected, half of the detection limit was used in the calculations.

Semi-volatile analyses were limited to monthly sampling because semi-volatiles quantified using Method 8270 in the recycle groundwater are also quantified by the volatile analysis (the dichlorobenzenes and trichlorobenzenes are quantified by weekly VOC analysis using Method 8260). Low ug/l levels of 10 other semi-volatile organics were quantified and

tracked in the recycle groundwater using Method 8270. Eight (8) of these 10 analytes were reduced to non-detect levels over the course of the study. These compounds are listed in **Table 4.2**, with the groundwater concentrations at the study outset and after 720 days of active treatment. Calculations to determine the degradation rates for these contaminants were not made because their detections in groundwater were sporadic and they were not quantified in the soil samples.

Figure 4-1 Biopilot Test Cell Extracted Groundwater Sum of Volatile Target Analytes - mg/l

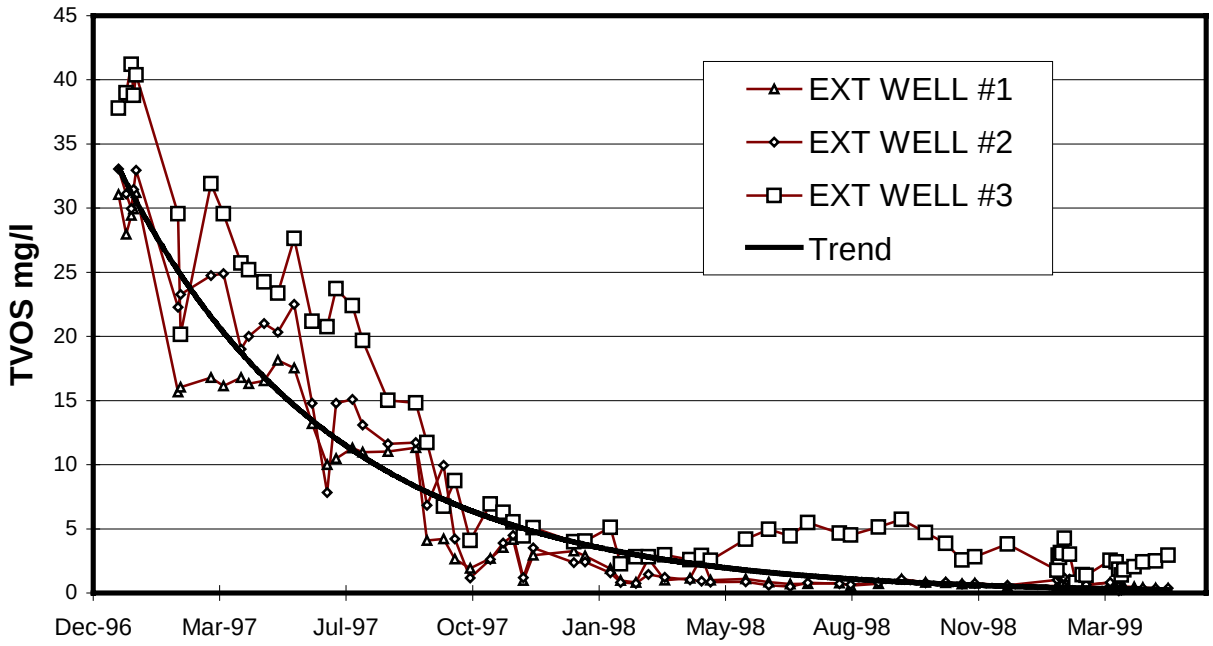


Figure 4-2 Biopilot Test Cell Extracted Groundwater Major Contaminant Concentrations (mg/l)

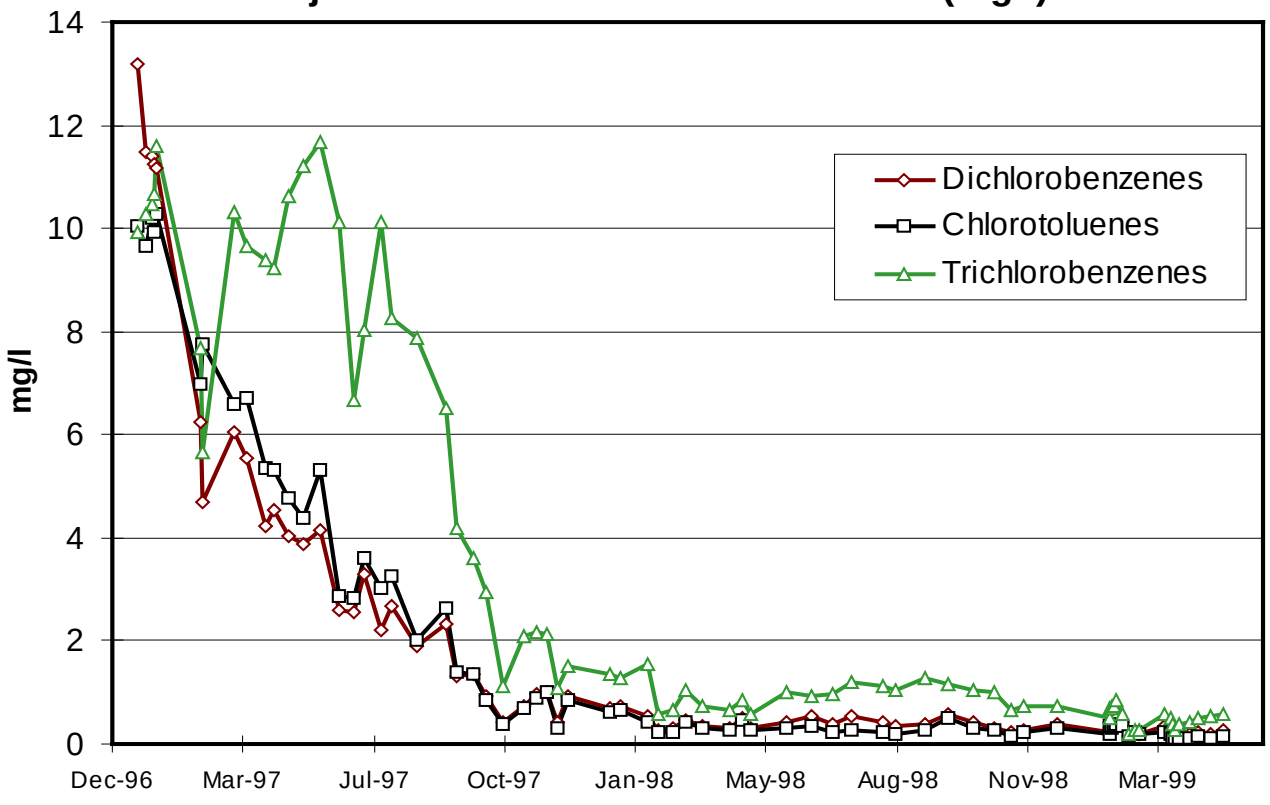


FIGURE 4.3
EXTRACTION WELL #1 GROUNDWATER MOLE FRACTIONS (%)

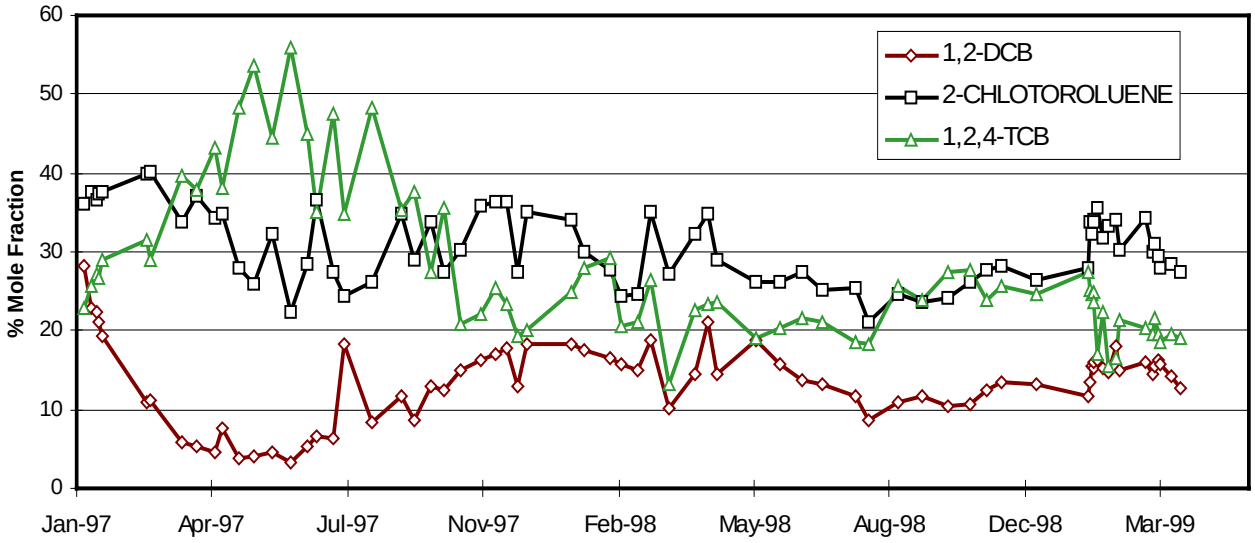


FIGURE 4.4
EXTRACTION WELL #2 GROUNDWATER MOLE FRACTIONS (%)

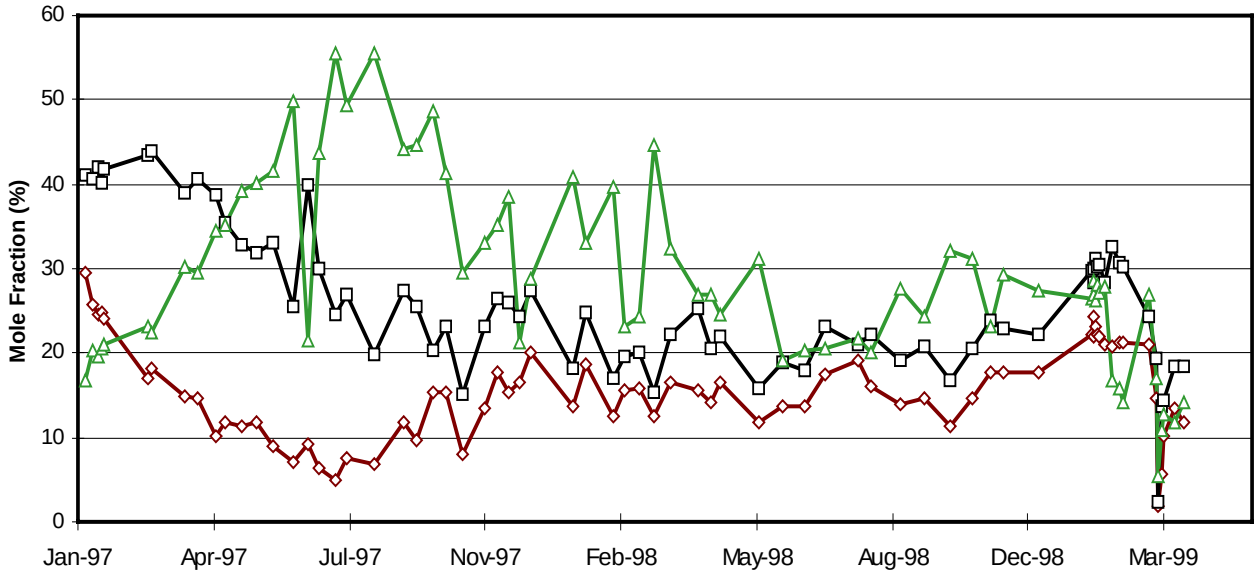
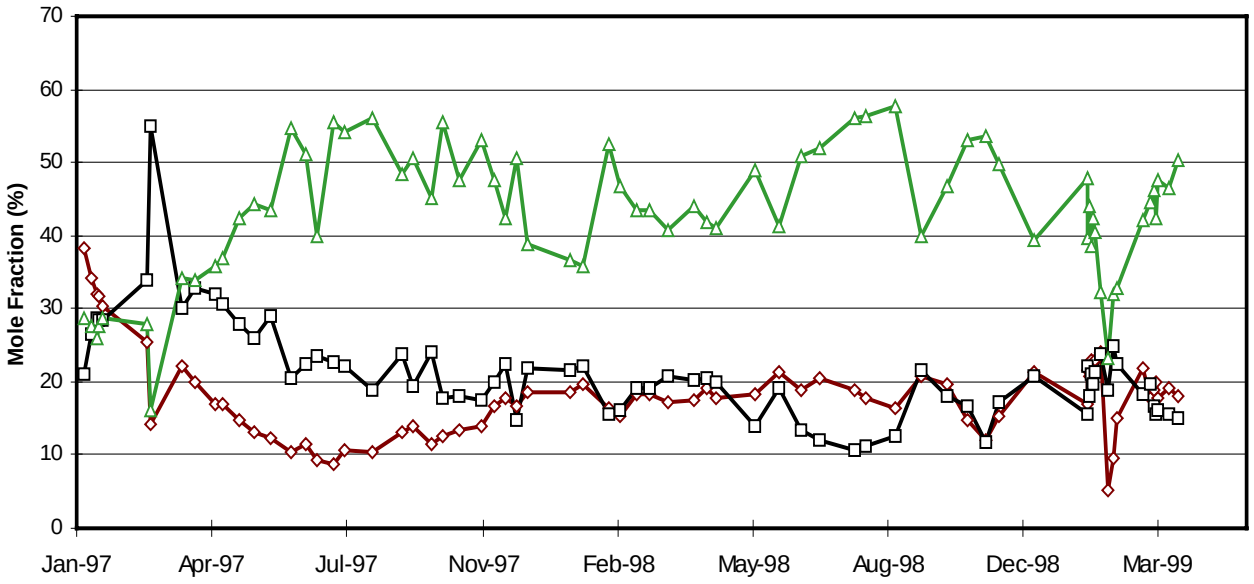


FIGURE 4.5
EXTRACTION WELL #3 GROUNDWATER MOLE FRACTIONS (%)



Shifts in mole fractions that were evident for the first 100 days of operation stabilized for the study duration. Increasing 1,2,4-trichlorobenzene and decreasing 1,2-dichlorobenzene mole fractions were consistent among all three extraction wells. The 2-chlorotoluene also exhibited a decreasing trend. Extraction Wells 1 and 2 exhibit less 1,2,4-Trichlorobenzene mole fraction dominance than Extraction Well 3 at the current low target analyte concentrations. The significantly higher TCB mole fraction in Extraction Well 3 is an effect of heterogeneity of the contaminant distribution within the treatment cell.

Throughout the course of the study the trends for contaminants in the groundwater were consistent. The concentrations of all the target analytes decreased significantly, most by an order of magnitude. This concentration and mole fraction data for the three major contaminants indicate that the relative solubility of these three compounds had decreased as a result of degradation of the readily accessible contaminants in the biopilot cell.

4.1.2 Dissolved Chloride Concentration

Increasing chloride ion mass in the groundwater is the most compelling evidence of biological degradation occurring within the treatment cell. Chloride concentration

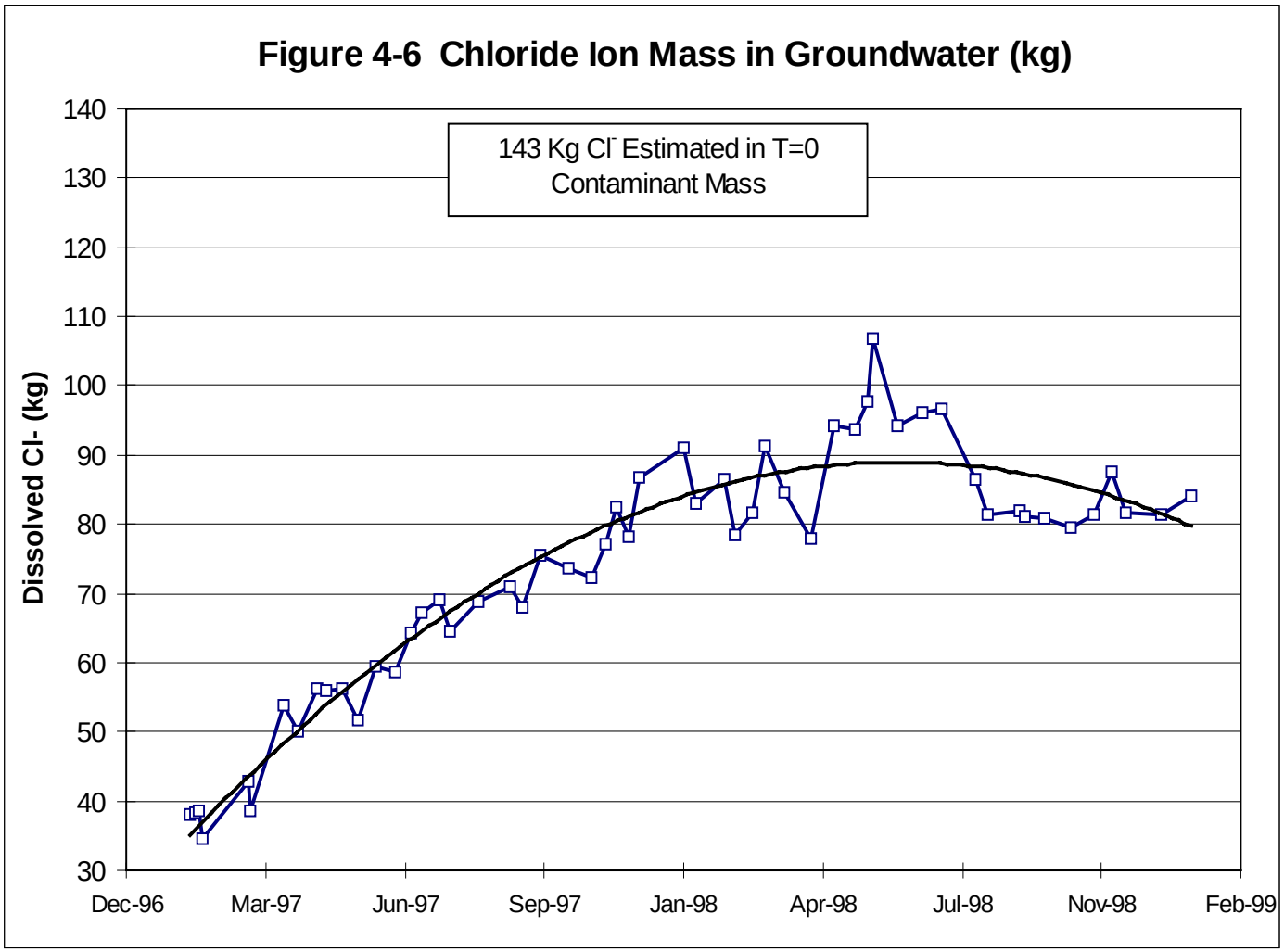
measured in the three groundwater extraction wells after the initial start up period (30 days) was approximately 285 mg/l. This was already significantly higher than the groundwater outside of the treatment cell, indicating that degradation of contaminants had commenced at start up of the system, without significant acclimation time. The current chloride concentration in the perched water outside of the cell is 20 mg/l. The mean chloride ion concentration in the Upper Cohansey perched water in the Former South Dye Area surrounding the biopilot cell during the study period was 45 mg/l. Chloride ion within the treatment cell increased to levels as high as 900 mg/l during the first year of operation, indicating that significant degradation had occurred.

Although variation in chloride measurements was expected, all three wells indicated significant increase in concentration over the first 12 months of operation. To estimate the mass of contaminants that had been degraded, the mean groundwater chloride ion concentration in the biopilot cell and water level measurements within the cell were used to calculate the mass of dissolved chloride ion.

Based on the initial soil estimates, 142 kg of chloride was incorporated in the initial measured contaminant mass in the biopilot cell. This estimate was calculated using the percent chloride of each contaminant that was quantified in each of the 125 soil blocks within the treatment cell (each soil block was represented by a pre-characterization sample). The maximum mean chloride ion concentration measured in May 1998 indicated approximately 107 kg of chloride ion had been released into the groundwater by degradation of contaminants. After this maximum value, the chloride ion concentration in the biopilot groundwater leveled off and the rate of increase observed over the first year of operation was no longer maintained.

Figure 4.6 indicates that the rate of chloride release to groundwater in the treatment cell remained high for the first year of operation. The second operating year showed a very low rate of chloride ion increase. The quantitation of dissolved chloride was complicated by increasing water retention within the unsaturated zone. The system was shut down and the water allowed to drain and equilibrate before measuring the level in the monitoring wells to determine how much water was actually in the treatment cell. The stagnation time needed for the water to equilibrate increased over time, and the amount of water

retained in the unsaturated zone also appeared to increase. During the later operational period the water table measured in the monitoring wells indicated a water table 14 feet below the surface, but after allowing the vadose zone to drain for 72 hours the saturated thickness increased another 3 feet. This water retention was not evident in the early months of operation, and is most likely the result of deposition of fine materials coming from the extraction wells and some biological growth in the soil pore spaces near the trench surface.

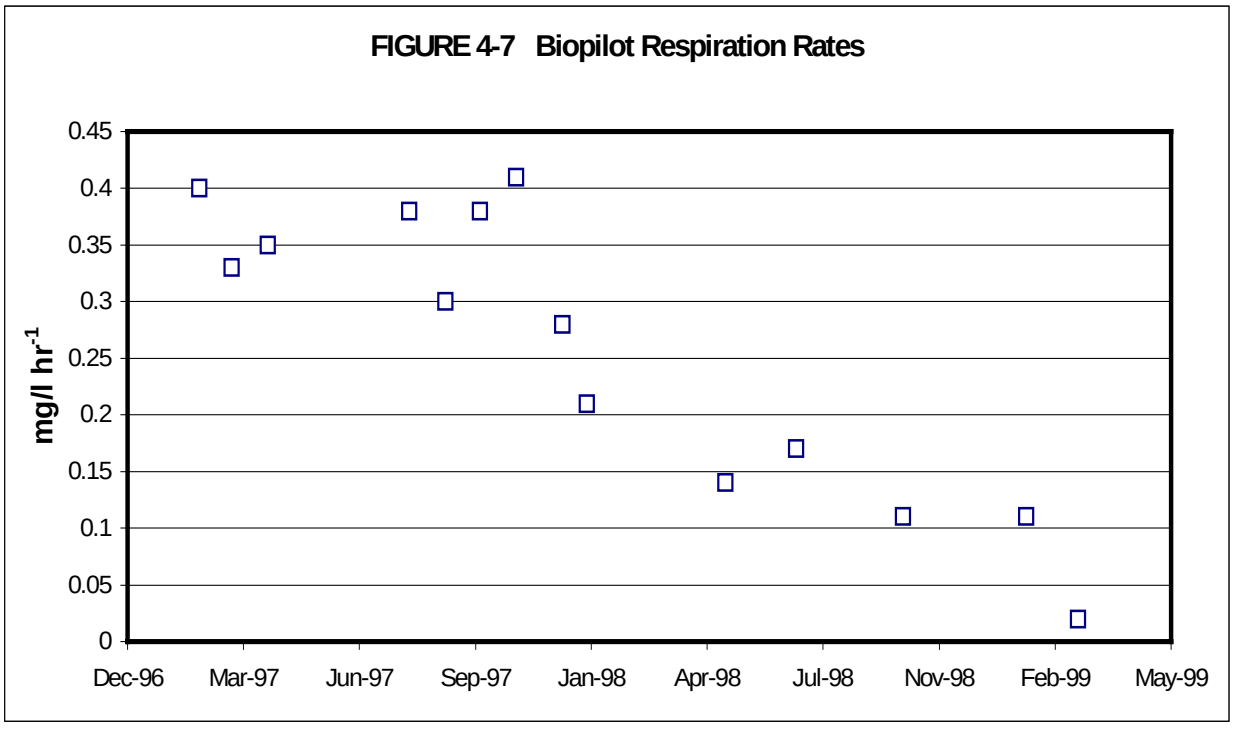


The ion chromatography method used for chloride quantitation required a high dilution factor (250x) due to the elevated chloride concentrations. A titration method using silver nitrate was used to analyze chloride samples without dilution, to check on the accuracy of

the chromatographic method. Analyzing duplicate samples by the 2 methods produced comparable results, indicating the dilution inherent to the ion chromatography method was not significantly influencing the results.

4.1.3 Dissolved Oxygen and Carbon Dioxide

The uptake of oxygen was measured by the system inputs, which were dissolution of high partial pressure oxygen into the recycled groundwater and sparging directly to the bottom of the cell through two sparge wells. The volume of oxygen delivered into the contactor tube was known, as was the volume sparged on a daily basis. The oxygen uptake rate was monitored directly by terminating oxygen delivery and tracking the rate of dissolved oxygen depletion in the groundwater. Plots of oxygen uptake by the cell were produced using the in line sensors, which recorded dissolved oxygen at fifteen minute intervals. Pounds per day oxygen utilization based on this rate was calculated using the mass of water within the cell, measured directly by monitoring well water level measurements. **Figure 4-7** presents the rate of dissolved oxygen uptake in the recycled groundwater over the course of the study. Each point on the graph is a separate oxygen uptake test performed on the cell.



Carbon dioxide was measured in the recycled groundwater and the unsaturated zone soil gas. Dissolved CO_2 remained consistent at 75 to 100 mg/l in all three extraction wells.

4.1.4 Soil Gas Oxygen and Carbon Dioxide

The soil gas profile for CO_2 was consistent among the three pairs of soil gas probes (5 and 10 ft. BGS). Lower oxygen concentration (< 5%) and higher CO_2 concentration (12% to 15%) were measured in the upper portion of the unsaturated zone, close to the surface seal.

4.2 POST TREATMENT SOIL SAMPLING RESULTS

Monitoring of groundwater VOCs and Cl^- during the course of the study eventually indicated that sampling of soils was appropriate, and this work was undertaken in May of 1998. The approved Work Plan described a midpoint sampling event after approximately nine months of operation, but based on the dissolved chloride data the sampling event was delayed in order to target sampling at a time close to or slightly past 50% degradation of the contaminants in order to make the best use of the data. Developing degradation rates for the contaminants in the active biological system requires at least three sample points spaced sufficiently to provide data that defines the true shape of the expected first order decay function.

One hundred twenty five (125) samples were collected on roughly the same plan view sample grid as the initial data set, offset approximately 1.5 feet horizontally in a westerly direction from the original borings. The initial borings did not deviate from vertical to any measurable extent, so an offset of 1.5 feet was sufficient to avoid encountering fill sand from an initial boring.

The midpoint data set indicated significant reductions in the soil had occurred. Basic statistical analysis of the data indicated that as much as 80% of the 1,2-dichlorobenzene, 62% of 2-chlorotoluene and 53% of 1,2,4-trichlrobenzene had been degraded from the starting soil mass.

The midpoint data indicated that these samples had been collected beyond the point of 50% reduction for 2 of the three major contaminants in the cell. Operation of the system was

continued for another eight months before the soil in the cell was sampled again. During this last 8 months of operation the groundwater parameters that had previously indicated that degradation was occurring appeared to level out and no longer indicated significant contaminant degradation. Dissolved chloride ion concentration no longer increased, and the groundwater target analyte concentrations leveled out and remained constant at approximately 4% of the starting concentrations.

Because of the possibility that the system had become dissolution limited with respect to contaminant availability to the groundwater, the operation was continued in an attempt to collect as much data as possible within the time constraints of the study. A final soil sample event was conducted in January 1999, using the same plan view sample grid as the previous two events, offset 1.5 feet in a easterly direction from the original sample locations. The locations of the borings for all three sample events are indicated in **Figure 4-8.**

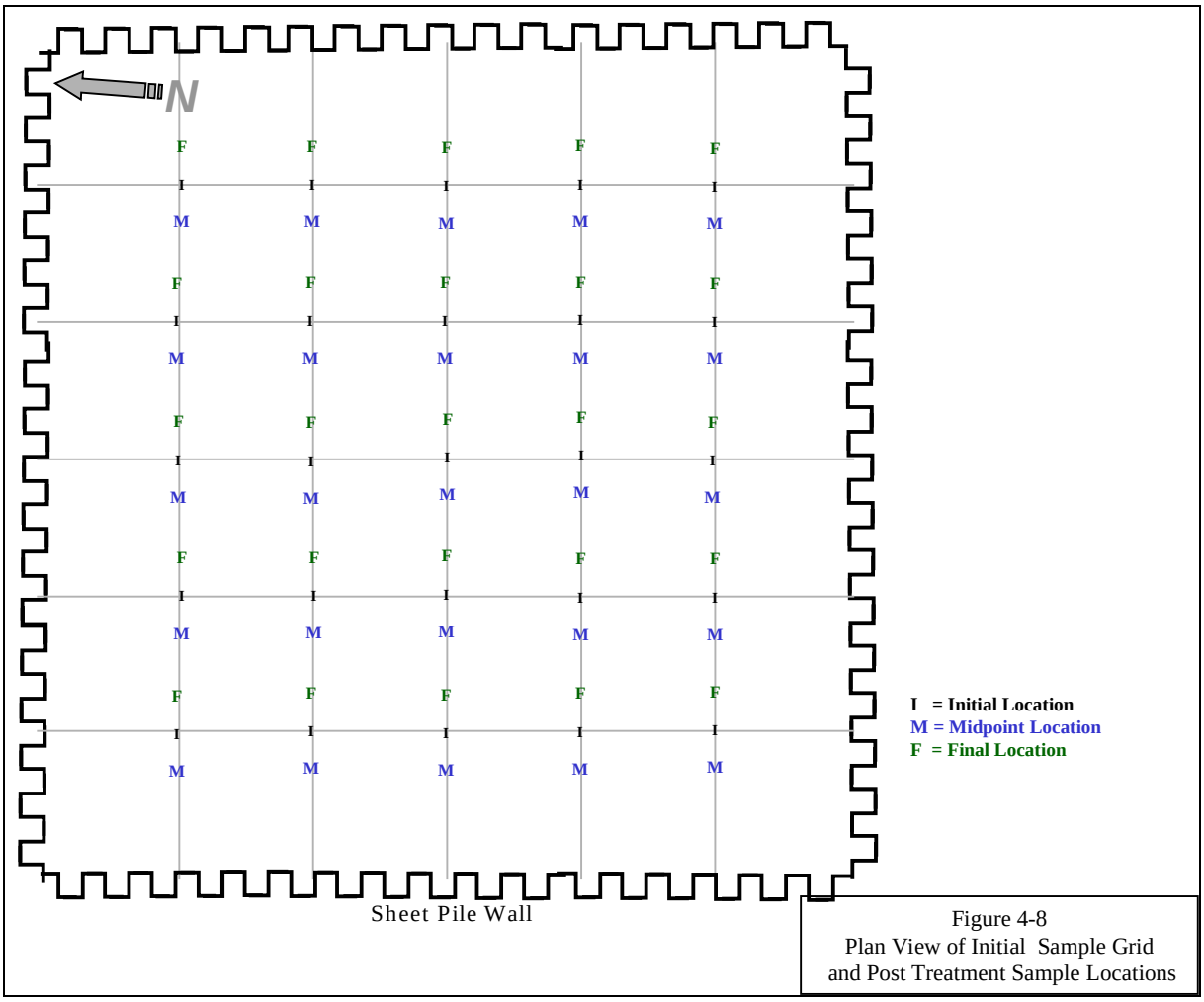


Figure 4-8
Plan View of Initial Sample Grid
and Post Treatment Sample Locations

Analysis of the data from the final soil sample event indicated that biodegradation had not significantly reduced the soil contaminant mass since the May 1998 sample event. As a whole, the final data set indicated more mass of contaminants in the cell than there was based on the midpoint sample event. This type of result is not entirely unexpected due to the difficulties in collecting reproducible soil samples because of heterogeneaities in soil properties and contaminant distributions on a very small spatial scale.

Because the system did not exhibit significant degradation during the second year of operation based on both groundwater and soil data, the midpoint and final soil samples were considered duplicate sample events. The focus of the biopilot was to collect data that would indicate what types or degradation rates to expect *in-situ* during biological

treatment. Both the midpoint and final soil sample events appear to have been undertaken after the end of the high activity period, and therefore represent two sets of samples collected after that phase of treatment. For comparisons of soil data before and after the high activity period of treatment, the mean of the midpoint and final sample data has been compared to the initial soil data collected before treatment.

The statistics based on the results of the initial and two post treatment soil sample events are compiled for 2-chlorotoluene, 1,2-dichlorobenzene and 1,2,4-trichlorobenszene in **Table 4-3.** The percent removals for the three contaminants in Table 4-3 are based on a comparison between the initial sample data and the mean of the midpoint and final sample data sets. The midpoint and final sample event data sets were combined to develop a mean value representing the soil concentrations that remained after a period of active treatment.

Table 4.3 Soil Data Comparison for Biopilot Cell Major Contaminants (mg/kg)

	1,2-DCB$_{initial}$	1,2-DCB$_{midpoint}$	1,2-DCB$_{final}$	1,2-DCB$_{mean\ m/f}$
Total Mass (kg)	**83**	**18**	**37**	**27.3**
Minimum (mg/kg)	0.1	0.01	0.04	0.03
Maximum (mg/kg)	1100	337	547	442
Arithmetic Mean (mg/kg)	66	13	30	21
Standard Deviation	170	38	80	59
	2-CT$_{initial}$	2-CT$_{midpoint}$	2-CT$_{final}$	2-CT$_{mean\ m/f}$
Total Mass (kg)	**53.8**	**20.3**	**29.4**	**24.9**
Minimum (mg/kg)	0.1	0.01	0.02	0.01
Maximum (mg/kg)	930	283	416	349
Arithmetic Mean (mg/kg)	50	14.8	23.2	19
Standard Deviation	129	44	59	51
	1,2,4-TCB$_{initial}$	1,2,4-TCB$_{midpoint}$	1,2,4-TCB$_{final}$	1,2,4-TCBm$_{ean\ m/f}$
Total Mass (kg)	**133**	**62**	**99**	**80.5**
Minimum (mg/kg)	0.2	0.11	0.07	0.09
Maximum (mg/kg)	1500	375	1888	1131
Arithmetic Mean (mg/kg)	101	43	72	57
Standard Deviation	212	76	245	161

Removal Percentages

1,2-Dichlorobenzene	**67%**
2-Chlorotoluene	**54%**
1,2,4-Trichlorobenzene	**39%**

Soil sampling provided a "before-and-after picture" of contaminant mass in the subsurface volume subjected to bioremediation. To determine biopilot treatment efficiency, statistical hypothesis tests were used to evaluate the significance of differences between the initial and final concentrations for the three major contaminants (1,2,4-Trichlorobenzene, 1,2-Dichlorobenzene and 2-Chlorotoluene). The null hypothesis is that the initial and final concentrations are equal (i.e., there was no treatment); the alternative hypothesis is that the initial concentration exceeds the final concentration.

An important factor to consider in the analysis of each contaminant is the frequency of values in different ranges of concentration, called the *concentration frequency distribution*. A plot of concentration vs. frequency in the shape of a bell-curve, with the middle of the curve representing the mean (average) concentration, represents a normally distributed set of data. If both the initial and final contaminant concentrations are "normally" distributed, a Student's t-test can be used to evaluate the null hypothesis. Alternatively, a nonparametric method such as the Wilcoxon Matched Pairs test or the Sign test is required. The Sign test computes the number of times across subjects that the value of the first variable is larger than the second variable. Under the null hypothesis (i.e., the two variables are not different from each other) this is expected to be the case about 50% of the time. The Wilcoxon Matched Pairs test assumes that the variables under consideration were measured on a scale that allows the rank ordering of observations, and subsequently, the rank ordering of differences between variables. If the magnitudes of differences contain meaningful information, then the Wilcoxon Matched Pairs test is more powerful than the Sign test. For this study, the probability that the sample data is normally distributed was tested by visual examination of the data using a histogram (i.e., a graph that shows the frequency distribution of a variable) and the Shapiro-Wilks' W test. The Shapiro-Wilks' W test is the preferred test of normality because of its good power properties as compared to a wide range of alternative tests.

Evaluation of the sample distribution for each contaminant strongly suggested that the soil data were not normally distributed. The histograms for each contaminant showed that the distributions were typically asymmetrical and bimodal. More significantly, Shapiro-Wilks' W test results (p-levels) were significant for each distribution ranging from 0.31 to 0.47 for the before treatment samples, and from 0.42 to 0.53 for the after treatment samples. Therefore, the Wilcoxon Matched Pairs test, instead of a Students' t-test was used to evaluate the data. The results of these tests are shown in Table 4-4.

Table 4-4
Statistical Analysis of Biopilot Cell Major Contaminants Using the Wilcoxon Matched Pairs Test

Parameter	Mean Initial Conc. mg/kg	Mean Final Conc. mg/kg	Mean Difference mg/kg	p-level
1,2,4-Trichlorobenzene	101.1	56.8	44.3	<0.01
1,2-Dichlorobenzene	62.0	20.0	42.0	<0.01
2-Chlorotoluene	42.8	18.0	24.8	<0.01

The STATISTICA™ system was used for all statistical analyses.

The p-levels show that the mean difference in concentration is highly significant for each contaminant. That is, the p-level represents the probability of error that is involved in accepting the observed loss of contaminant. At the levels indicated, the probability of error is much less than 1% for all the parameters. Thus, the null hypothesis (i.e., no treatment) should be rejected, and the alternative hypothesis, that the initial concentration exceeds the final concentration, should be accepted. Biopilot cell mass removals and treatment efficiency are summarized in Table 4-3.

Figures 4-9 through 4-11 indicate mass reductions measured in soil for the three major biopilot contaminants. These figures separate the data into the 6 foot vertical layers that were represented by the composite samples. The reported contaminant reduction is based on a comparison between the initial soil mass and the mean of the midpoint and final soil mass estimates. The mass of each contaminant was calculated using the measured concentration of each contaminant multiplied by the soil mass in each of the 125 soil blocks that are represented by a sample. A summation of the blocks provides an estimate for the entire cell. The difference between the contaminant mass before and after treatment was calculated by this method and reported as a percent removal. A simple comparison of the means of the two data sets provides a similar value for contaminant reduction, although the summation of soil blocks provides a higher level of precision.

Figure 4-9 Biopilot 2-Chlorotoluene Mass in Soil
52% Removal

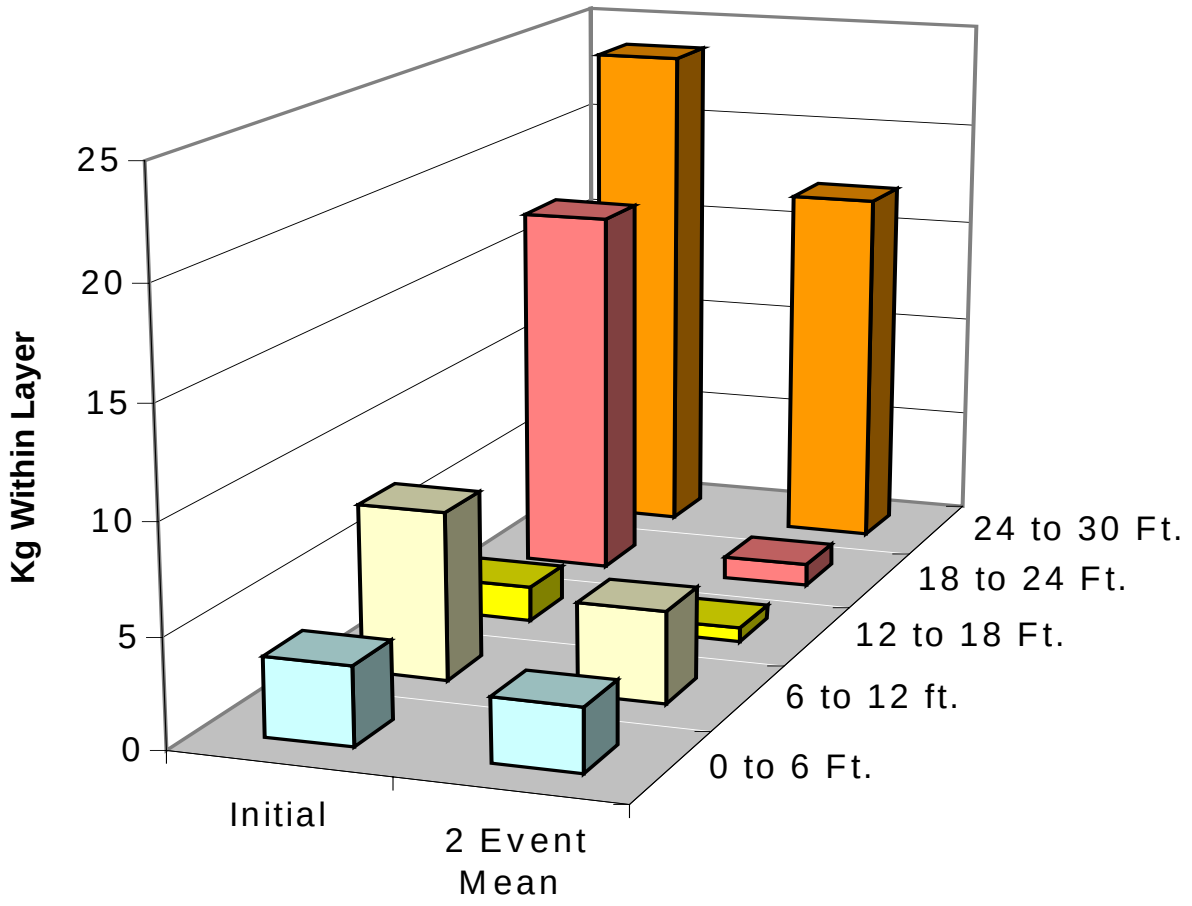


Figure 4-10 Biopilot 1,2-Dichlorobenzene Mass in Soil
67% Removal

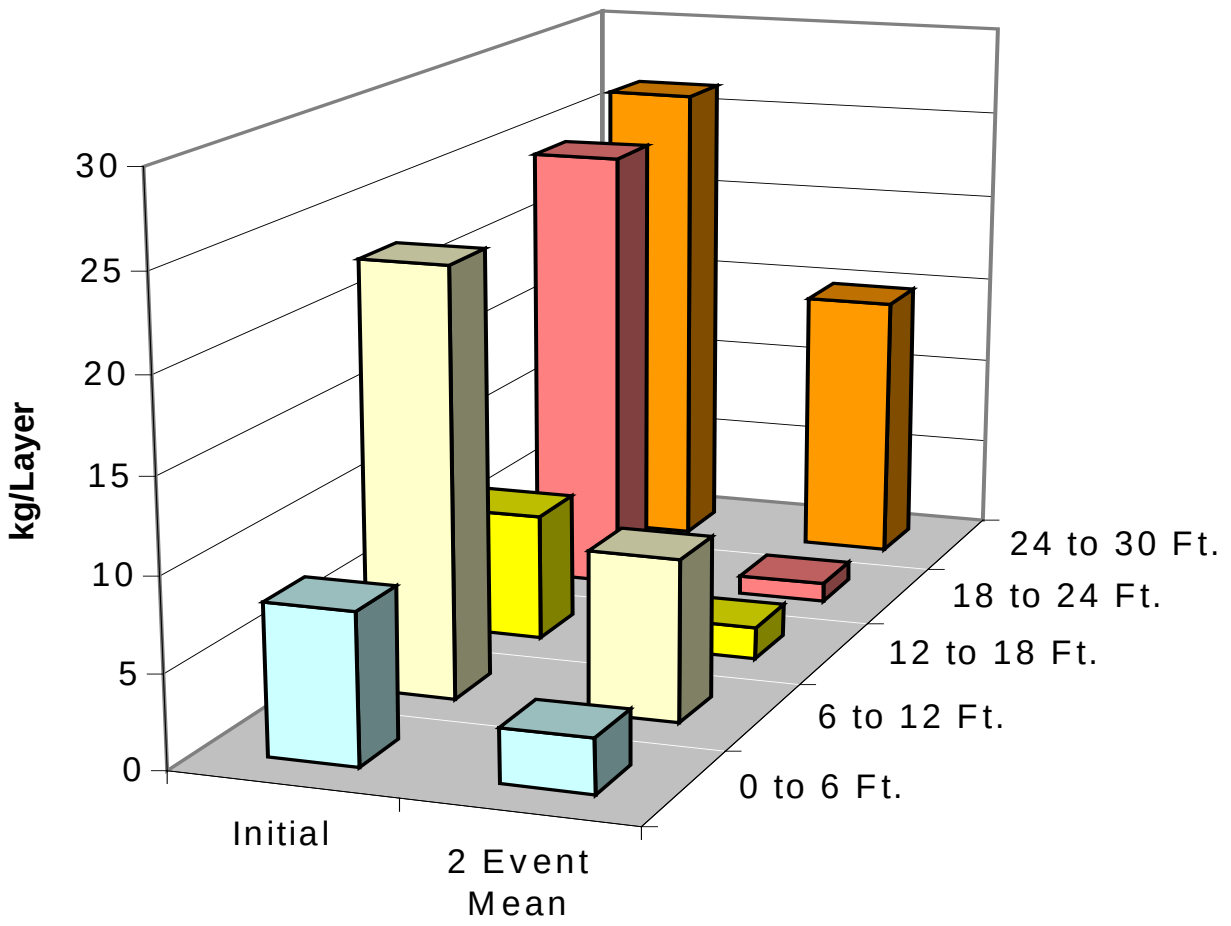
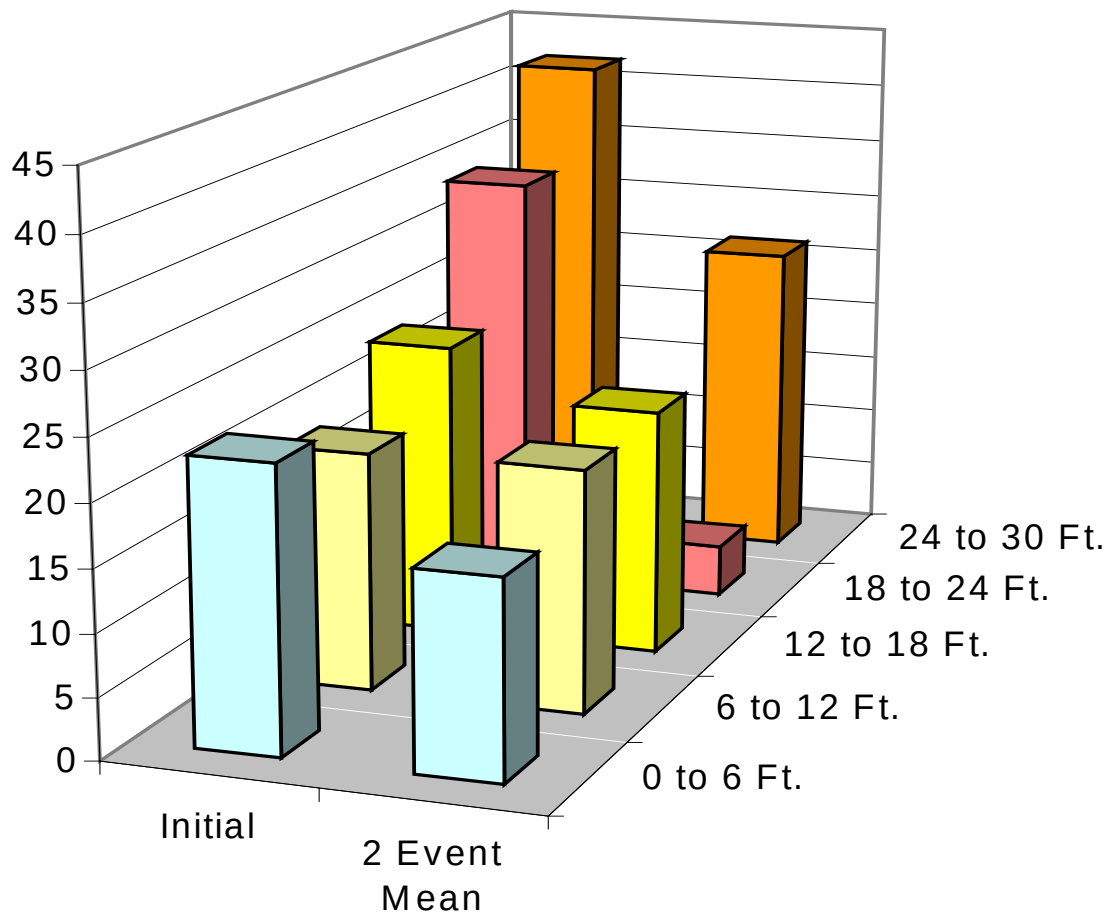


Figure 4- 11 Biopilot 1,2,4-Trichlorobenzene Mass in Soil 40% Removal



From Figures 4-9 through 4-11 it is apparent that the majority of the biodegradation occurred in the sandy zone from 18 to 24 feet below grade. This layer resides just above the silt and clay stringers at the cell bottom and likely contained the highest concentrations of contamination that were readily available to the groundwater.

The removal of the minor (< 2% of the total coil contaminant mass) soil contaminants has not been calculated because the three sample events had different detection limits, which were based on dilutions that were necessary because of the concentrations of the major contaminants. High concentrations of the three major contaminants in the initial data set resulted in elevated detection limits for the minor components. For the minor components, estimated differences before and after treatment would be based more on half the detection limit for the initial data set than actual measurements. Estimating removal based on half of the detection limits would not be basing the estimation on accurate information.

It is likely that the biological system was able to rapidly degrade the contaminants that were readily available to the groundwater, after which the slow dissolution of the remaining mass limited the activity. The rate of degradation is a related to the rate of dissolution into the groundwater. Other possibilities for the decline in the rate of degradation after the first year of operation include the accumulation of inhibitory by-products such as chlorocatechols that could limit the enzymatic activity of the contaminant degrading cultures. This possibility was investigated by sampling for the chlorocatechols that would be produced by the aerobic degradation of the chlorotoluenes, dichlorobenzenes and trichlorobenzenes in the biopilot cell. None of the five chlorocatechols tested for were detected in the biopilot groundwater, with detection limits of 50 ug/l.

4.3 SYSTEM OFF GAS ANALYSIS AND PROJECTED VOLATILIZATION

A passive off gas venting system was installed at the time of construction, but it did not function as expected. The pea gravel layer beneath the surface seal was too thin and appeared to clog with fines from above. Off gas escaped through leaks in the liner system where resistance was less than the approximately 1" of water pressure required to exit through the passive vent. This back pressure in the vent system was created by the volume measuring device. Attempts were made to determine where the off gases were escaping by measuring the hydrocarbons in the air just above the ground surface during

and after sparge events, when off gases would have been forced out of the system. The portable photoionization detector did not detect measurable concentrations of VOCs anywhere above the liner during this investigation. This indicates that gases did not escape through a single opening in the system, but escaped slowly through several locations.

The shallow soil gas was sampled to determine the potential for volatilization losses from a full scale system. The volume of off gas generated would be equal to the system sparge gas input, which was known. As a conservative measure, the soil gas close to the surface was sampled using suma canisters and these samples used to represent off gas concentrations. Sampling of soil gas and taking that concentration to represent what would come out at the ground surface is conservative because it does not account for any channeling losses where sparged oxygen escapes to the surface without contacting much contamination, and the shallow soil gas sampling probes were installed at a depth of 5 feet. The soil gas sampled was in equilibrium with the soil contamination, but the actual gas escaping to the ground surface would in all probability be less than this concentration because of a non-equilibrium condition between the sparged gas and the contaminants. Table 4-5 reports the volatilization estimates for the contaminants based on volumes of gas sparged and the measured concentrations in soil gas beneath the surface liner.

TABLE 4-5

Projected Volatilization

Analytes	pbbv	mol/day	$Q_{off\text{-}gas}$ (liters/day)*	mol. wt.	lbs/day	lbs/yr
1,1-Dichloroethane	131.7	0.000012	2100	98.97	5.70E-05	0.0208
1,1,1-Trichloroethane	1723	0.000162	2100	133.42	7.46E-04	0.2724
Trichloroethene	1159	0.000109	2100	131.4	5.02E-04	0.1832
Tetrachloroethene	706.3	0.000066	2100	165.85	3.06E-04	0.1117
1,1,2,2-Tetrachloroethane	144	0.000014	2100	167.86	6.24E-05	0.0228
1,3-Dichlorobenzene	13.72	0.000001	2100	147.01	5.94E-06	0.0022
1,4-Dichlorobenzene	13.93	0.000001	2100	147.01	6.03E-06	0.0022
1,2,4-Trichlorobenzene	15.35	0.000001	2100	181.46	6.65E-06	0.0024

* Based on amount of oxygen sparged into the biopilot cell.

0.618 total estimated volatilization losses (pounds/year)

Based on the results in **Table 4-5**, the data indicate that significantly less than 0.1% of the initial soil contaminant mass would be lost to volatilization over the course of an operating year. This level of volatilization did not produce levels of contaminants that could be measured above the ground surface. A full-scale system would be designed to minimize volatile losses and incorporate engineering controls to address any contaminants in off gases, should it be necessary. The biopilot project was implemented in the most contaminated portion of the South Dye Area, and was designed to provide oxygenation and mixing in a aggressive manner due to time constraints. Because of these factors the volatilization effects are maximized and of a worst case nature. This extrapolation overestimates the mass that could volatilize to ambient air from a source are, but still indicates that even without engineering controls and using an aggressive oxygenation system the amounts of contaminants released to the atmosphere are too small to measure directly.

4.4 MONITORING OF CONTAMINANT REBOUND IN GROUNDWATER

After determining to what rate and extent the contaminants in the cell could be degraded by the aerobic biological system in a relatively short active treatment period, additional monitoring of the system focussed on what types of rebound effects could be expected in the groundwater. After 750 days of operation the oxygen delivery system was shut off and the rate of groundwater recycle reduced to produce a groundwater velocity similar to conditions outside of the cell in the Primary Cohansey, which is generally about 1 foot per day. The groundwater velocity in the Upper Cohansey where the cell was located depends solely on infiltration of precipitation, and therefore varies significantly. This test condition was designed to mimic a field condition where an active biological treatment had been applied and then the external stimulation (delivery of oxygen and nutrients) shut off. Figures 4-12 and 4-13 indicate that rebound was not evident in extraction well 1 or extraction well 2. The concentrations in extraction well 3 were still higher than the other extraction wells, but the concentrations did not increase significantly during the rebound test and were maintained at approximately 3% of the groundwater concentration at the start of the study. Overall, rebound effects did not appear significant based on the data.

Because the groundwater was recycled through the residual soil contamination over and over in the closed system, the resulting groundwater concentrations may have been higher than what would occur in a full scale system that would not incorporate the physical barriers used in the biopilot. Figures 4-12 through 4-14 present the groundwater data from the last 500 days of operation, beginning after the groundwater concentrations had been reduced during the first year of operation, and ending after 60 days of rebound test condition (reporting the tail end of the plot presented in Figure 4-2, for the individual wells). Figures 4-12, 4-13 and 4-14 are plotted on the same concentration scale for relative comparison among the three extraction wells.

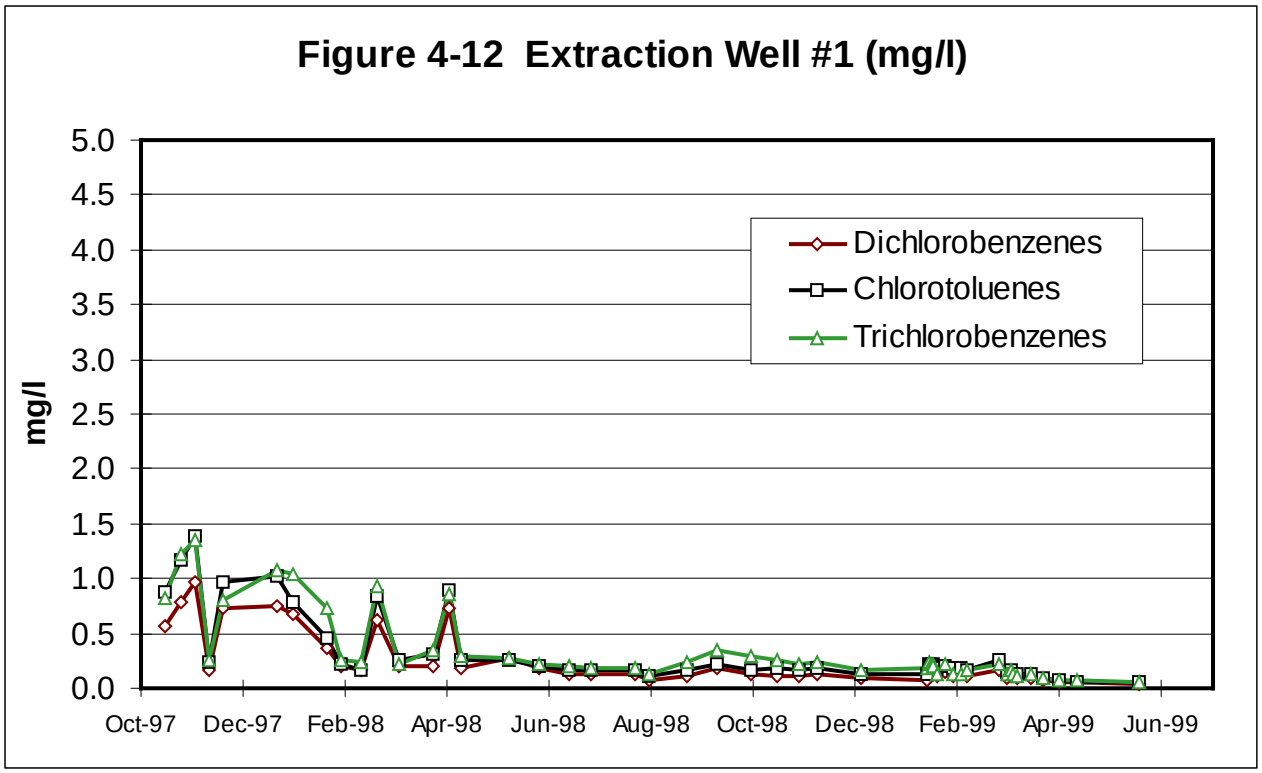


Figure 4-13 Extraction Well #2 (mg/l)

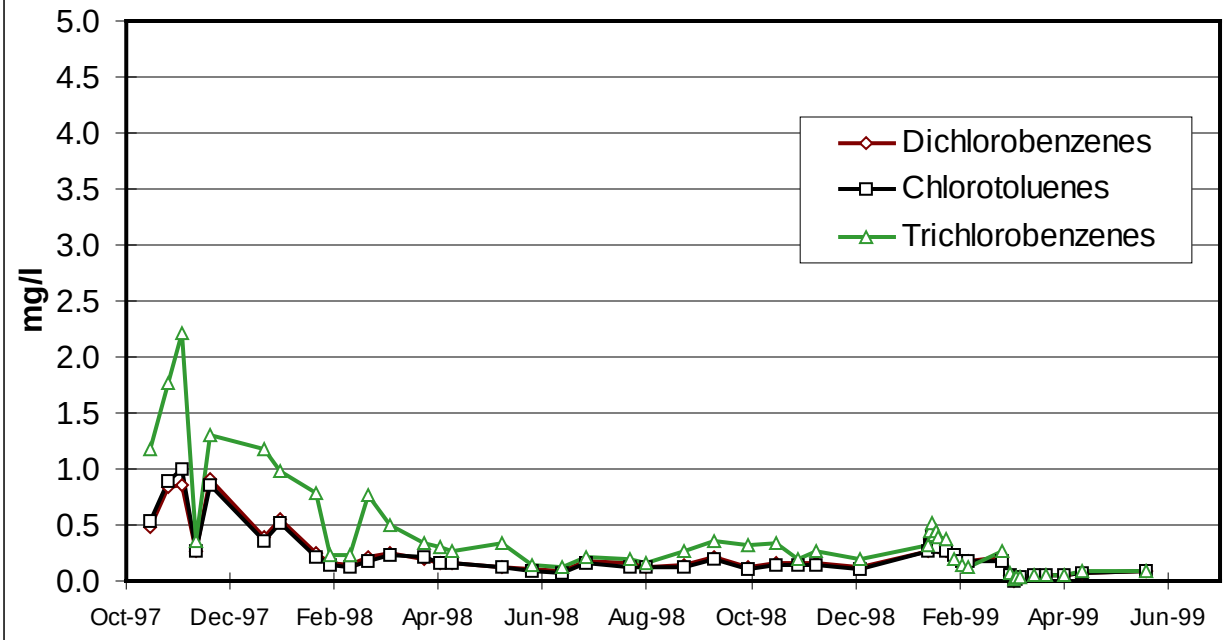
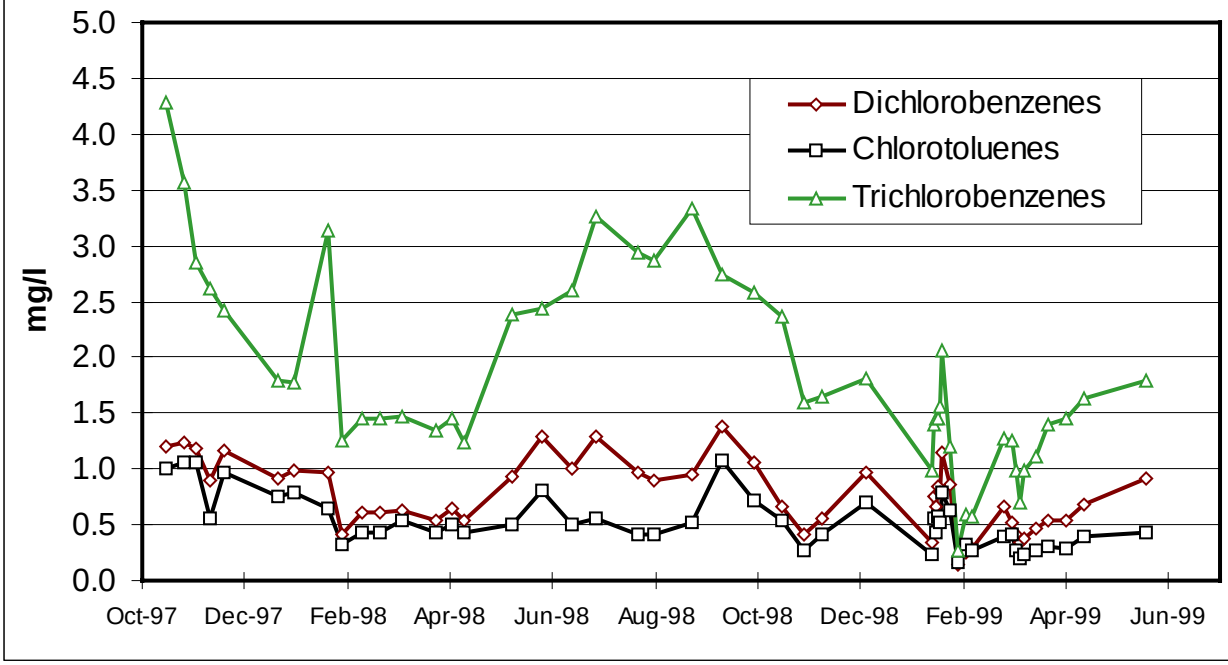


Figure 4-14 Extraction Well #3 (mg/l)



A second rebound test is being performed that incorporates a slow flushing of the cell with uncontaminated groundwater extracted from the bottom of the Primary Cohansey beneath the Former South Dye Area. The same slow flow conditions are being maintained as for the first rebound test, with no oxygen or nutrients delivered. Instead of recycling groundwater, the extracted groundwater is discharged back to the Upper Cohansey outside of the biopilot cell. The recharge of uncontaminated groundwater is delivered to the cell through the infiltration trench opposite the extraction wells at the same flow rate as extraction. The cell saturated thickness is maintained at approximately 15 feet, or half of the cell depth. This test was designed to produce conditions more similar to those in the field, where infiltrating rainwater seeps to the saturated zone and slowly moves through the area.

This second rebound test is ongoing and the data will be presented as it becomes available.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Based on the data collected during the course of the study and during monitoring of rebound effects, there were significant reductions in the mass of all three major contaminants in the soil. The effects of these removals were more pronounced in the groundwater concentrations. Removals in soil of 40 to 80 percent of the contaminants resulted in decreases in groundwater concentrations of greater than 95, and as high as 99.5 percent.

System performance and monitoring data validated the operating principles of the biopilot process design and demonstrated that the contaminants of concern could be removed using bioremediation. In the two years (i.e., 720 days) that the cell was operated, approximately 40% of the 1,2,4-Trichlorobenzene, 54% of the 2-Chlorotoluene and 67% of 1,2-Dichlorobenzene that was present in the soil at the beginning of the study was degraded. These data correspond to mean contaminant removal rates of 0.03 mg/kg-d for 2-Chlorotoluene and 0.06 mg/kg-d for both 1,2,4-Trichlorobenzene and 1,2-Dichlorobenzene. It is important to note, however, that the majority of contaminant removal, as tracked by chloride release, occurred in the first year of operation. During the second year of operation, chloride levels in the cell groundwater did not increase and the change in

dissolved contaminant concentration was minimal. A good estimate of the accessible NAPL is the contaminant mass removed during operation of the biopilot.

The reasons for the high removal rate declining after the first year of operation is most likely attributable to the system becoming dissolution limited with respect to contaminant release into groundwater. The accumulation of breakdown products to levels that would be inhibitory is unlikely. None of the chlorocatechols, which would be the breakdown products of the three major contaminants in the cell, were detected in groundwater samples analyzed at the end of the study. There were no pH fluctuations throughout the study, and dissolved oxygen and nutrients were available.

In-situ biological remedial technologies are faced with the same limitations inherent to all *in-situ* technologies that rely on fluid flow delivery for contacting the treatment amendments with the subsurface contaminants. Subsurface heterogeneities hinder uniform flow distribution in the subsurface and density differences between contaminants and water can result in completely different flow paths. This is apparent in the biopilot soil data, where rapid degradation was visible over the first year of operation, followed by a second operating year with significantly reduced biological activity. This is likely the result of biological degradation of the contamination readily available to groundwater, after which the availability of contaminants to groundwater (and biological activity) became dissolution limited. All *in-situ* remedial technologies that depend on fluid flow in the subsurface will suffer this same limitation.

6.0 SUPPLEMENTAL REPORT FOR THE BIOPILOT TRACER STUDY

6.1 INTRODUCTION

In January 1998 an investigation of the biopilot flow field was undertaken using a non-reactive tracer. This work was performed by Ciba, and approved by the EPA, to supplement and expand the monitoring plan presented in the project work plan. Prior to the tracer investigation, the biopilot had operated for more than a year without interruption.

The primary objectives of the study were 1) to identify area(s) of the cell, if any, characterized by gross stagnation or short-circuiting, 2) to determine direction and velocity of cell flow, and 3) to establish cell hydrogeologic properties such as porosity. The tracer study proposal included both saturated and unsaturated flow characterization. The work was subsequently divided into two phases. In the first phase, the tracer was added to the saturated zone. Unsaturated flow characterization began with tracer introduction to the vadose zone after saturated zone concentration had equilibrated.

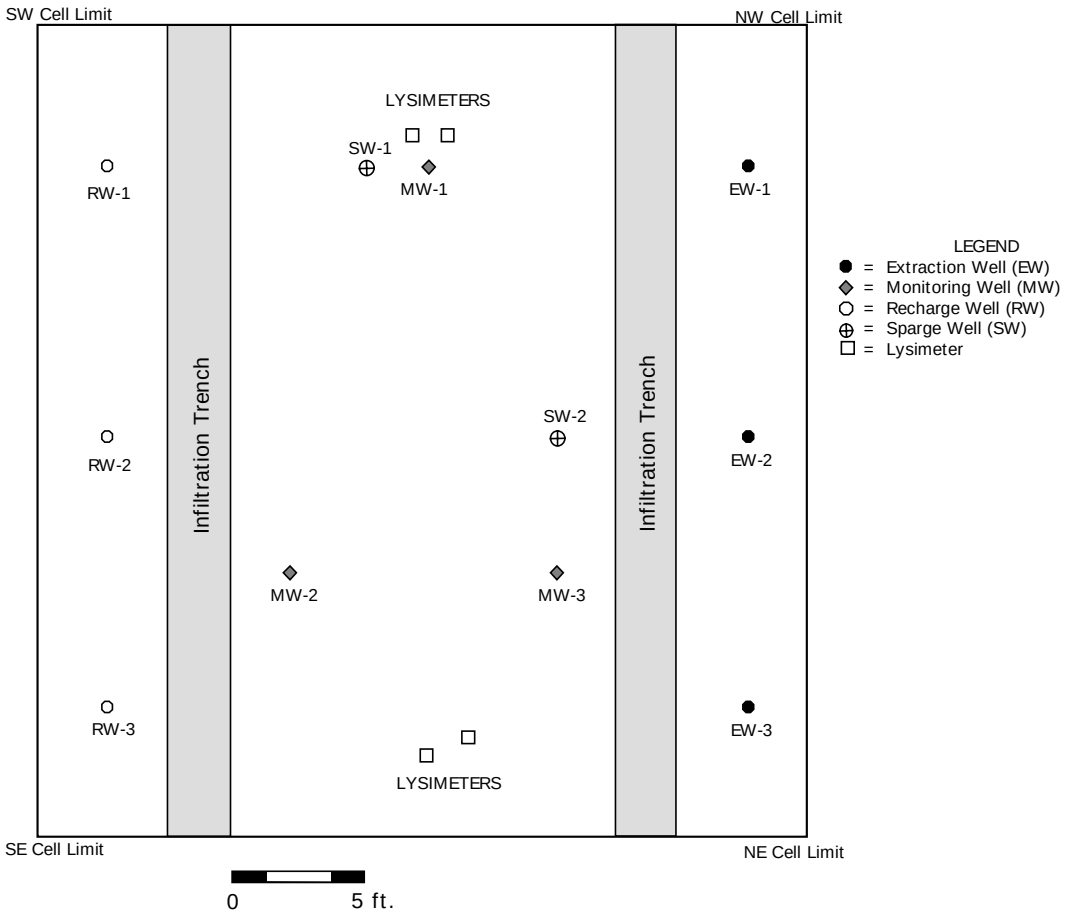
The tracer was introduced under normal operating conditions with only minor changes in system configuration. Tracer movement was observed by sampling the fluid circulation system and other cell components such as monitoring and sparge wells. Because of its ease of use and low background concentration, lithium (Li^+) was selected as the tracer. Li+ is chemically and biological stable and has no impact on microbial populations at low concentration. An important advantage of lithium for this study was that it could be quickly and accurately measured on-site using available instrumentation.

The biopilot water circulation system design was based on three dimensional, saturated/unsaturated fluid flow modeling. Model results indicated that a six (6) well recharge and extraction system, combined with two (2) infiltration trenches, would provide complete coverage throughout the cell. Typically, groundwater was extracted at the rate of 10 gpm with one-half of the flow returned directly to the saturated zone and the remainder

diverted to the trenches. Under these conditions, variations in hydraulic gradients across the cell are small. Tests and measurements conducted after system startup indicate that the cell does not leak.

Figure 1 shows the positions of all wells and monitoring components. The recharge and extraction wells are placed 2.5 feet from the edge of the barrier walls at 5, 15, and 25 feet along opposite sides of the system. The trenches, which are 2 feet wide, are located with centers at 7.5 and 22.5 feet along the surface domain running transverse to groundwater flow. The recharge and extraction wells are screened across the lower 10 feet of the cell. The monitoring and sparge wells have 5-foot and 6-inch length screens, respectively. Both types of wells are set immediately above the base of the clay. Lysimeters are installed in nested pairs at depths of 5 and 10 feet below ground surface.

FIGURE 1
BIOPILOT PLAN VIEW SHOWING WELLS AND MONITORING COMPONENTS



6.2 THEORETICAL CONSIDERATIONS

The experimental approach used for this study follows the methods explained by Maloszewski and Zuber (1982) and Grady and Lim (1980). Fluid or tracer elements passing through a non-ideal system such as the biopilot typically exhibit unique residence times. The mean age of water leaving the system (also called turnover rate) is known as the hydraulic residence time. Turnover rate (T) is defined as:

$$T = V/Q$$

where Q is the volumetric flow rate and V is the volume of water in the system. The mean transit or residence time (t_t) of a tracer is defined as:

$$t_t = \int_0^\infty tC_I(t)dt \; / \; \int_0^\infty C_I(t)dt$$

where C_I is the tracer concentration observed at the measuring point as the result of an instantaneous injection at time t = 0. The mean residence time of the tracer equals T (t_t = T) only if an ideal conservative tracer is both injected and measured in flux, i.e., when $C_I(t)$ in the above equation is the concentration observed for both injection and detection averaged by flow rates. If $C_I(t)$ is normalized to be independent of the quantity of the injected tracer, it is called the exit age-distribution function of the tracer. The exit age-distribution of the tracer is equal to the exit age-distribution of the system (generally known as the E(t) function) if the tracer behaves in an ideal manner and is measured in flux concentration (i.e., ratio of solute flux to volumetric fluid flux). Under these circumstances E(t) may be defined as:

$$E(t) = C_I(t) / \int_0^\infty C_I(t)dt$$

Because the entire tracer mass being measured must pass through the monitoring site from time 0 to infinity, the area under the distribution curve equals unity. It follows, then,

that the fraction of tracer which has a residence time between t and t + dt is E(t)dt. Thus the mean residence time of the tracer may be defined by:

$$t_t = \int_0^\infty tE(t)dt \,/\, \int_0^\infty E(t)dt = \int_0^\infty tE(t)dt$$

Tracer velocity which is equal to distance traveled divided by mean residence time can be computed by:

$$\upsilon = L \int_0^\infty 1/tE(t)dt$$

where υ is mean pore velocity and L is the distance between the tracer input and outflow or measuring point.

Either a step or instantaneous input may be used to obtain the point distribution or exit age-distribution of the system. The preferred approach is to obtain E(t) from experimental impulse data. E(t) is calculated by dividing $C_I(t)$ by the total amount of tracer flux at the measuring point. Total tracer mass is determined by integration of the tracer response curve. The mean residence time, then, may be determined by integration of the time-point distribution data. A numerical procedure such as Simpson's rule or the trapezoid rule is often used to perform the integration.

6.3 EXPERIMENTAL APPROACH

The tracer was introduced to the biopilot at the recharge wells as an impulse (instantaneous injection). Tracer movement within the saturated zone was tracked by analyzing extraction well discharge and samples from the monitoring and sparge wells. The horizontal distance of each sampling point from tracer entrance is given in Table 1.

In preparation for the tracer study, the biopilot groundwater circulation system was shutdown for 24 hours to drain the unsaturated zone and level the water table. The recharge well packers were then removed and small stainless steel (0.125 inch

I.D.) purge lines were placed in the monitoring and sparge wells for collection of groundwater samples. Each sample line was connected to a variable speed peristaltic pump which discharged to a collection jar.

Water levels at each monitoring point in the system were recorded immediately before the start of the study and while the study was underway. The water table position at the beginning and end of the study was 14.7 feet below ground surface. This indicates that the saturated zone depth was 15 feet given that the depth to cell bottom averages 29.7 feet below ground surface.

The tracer was added to the groundwater by pouring 71.5 L of 1,000 mg/L (as Li^+) solution directly into each recharge well. This resulted in the addition of 214,500 mg of Li^+ to the cell. Reagent grade Li_2CO_3 (Fisher Scientific) was used as the source of Li^+. Immediately following addition of the tracer, the recharge well packers were replaced and the extraction well pumps were started at a flowrate of 3 gpm each (total flow 9 gpm). For the first phase of the study, all extracted groundwater was returned to the injection wells. This configuration assured that tracer movement was limited to the saturated zone and that flux from the vadose zone did not dilute the tracer response.

TABLE 1
BIOPILOT WELL SAMPLING POSITIONS AND SCREEN INTERVALS

Well	Horizontal Distance From Tracer Input[1] (ft)	Screen Depth Below Ground Surface[2] (ft)	Screen Depth Below Water Table[3] (ft)
EW-1	25.0	20 - 30	5 – 15
EW-2	25.0	20 – 30	5 – 15
EW-3	25.0	20 – 30	6 – 16
MW-1	12.7	25 – 30	10 – 15
MW-2	7.2	25 – 30	10 - 15
MW-3	17.9	25 – 30	10 – 15
SW-1	10.0	>29	>14
SW-2	17.6	>29	>14

Before obtaining a sample from the monitoring and sparge wells, it was necessary to flush (purge)the sample lines for several minutes. Generally, the lines were purged for 15 minutes or more before samples were obtained; nonetheless, the amount of liquid removed from the system was relatively small due to the small diameter of the tubing. Samples were collected in glass bottles and preserved by addition of nitric acid to pH ≤ 2. All samples were analyzed for Li+ by atomic absorption spectrophotometry (Perkin Elmer 3100) using EPA Method 200 series protocol.

After the tracer passed through the system and the groundwater concentration equilibrated, approximately one-half of the groundwater flow was diverted to the trenches. Monitoring of the unsaturated zone and the trenches was then initiated. This effort failed to provide sufficient data for unsaturated flow field characterization because water levels in the trenches became unbalanced resulting in very low flow on one side of the cell. Because the vadose zone delivery was not uniform across the trenches during the tracer delivery, the second phase of the study was terminated.

6.4 RESULTS AND DISCUSSION

During the first 24 hours of the study, all monitoring points were sampled every 2 to 3 hours. In the second 24 hours of operation, the wells were sampled every 4 to 6 hours. Thereafter, the sampling frequency was reduced as the tracer passed by each monitoring point. After more than 165 hours of monitoring, the groundwater Li+ concentration had equilibrated at 1.4 mg/L and saturated zone sampling was discontinued.

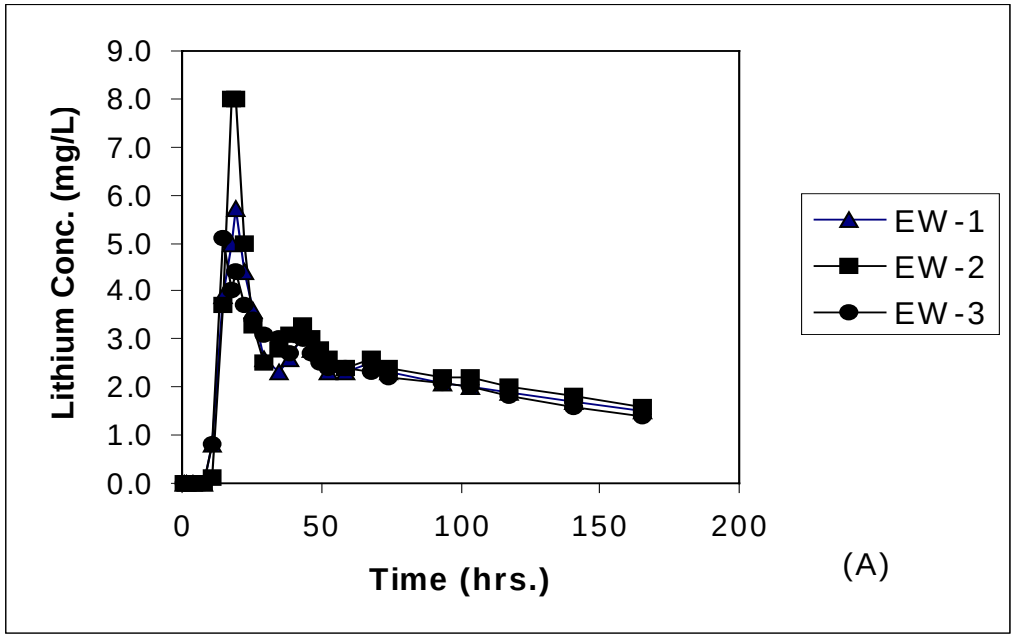
The tracer monitoring data are tabulated in the Appendices. The tracer first appeared in MW-2, the sampling point closest to the recharge wells, approximately eight hours after injection and startup of the recharge pumps. Two and one-half hours later, the tracer appeared at the extraction wells, and fifteen hours after startup the tracer appeared at MW-1 and MW-3. The peak tracer concentration in the extraction wells occurred 19 hours after cell startup. The tracer appeared at SW-1 after 29 hours of operation and at SW-2 approximately 38 hours after startup.

6.4.1 Biopilot Flow Field Characteristics

Tracer concentration response curves for the three extraction wells are plotted in Figure 2A. Note that the response curve for each well is very similar, varying only slightly in magnitude and time to maximum peak concentration. As shown by the secondary peak on the tail-end of each curve, tracer response was impacted by Li^+ circulation after approximately 35 hours of operation. A decreasing log-linear regression model based on the time-concentration data (corrected for equilibrium concentration) before and after the secondary peaks was used to correct each curve for this effect. Normalized response curves for the extraction wells are plotted in Figure 2B.

Results from analysis of the normalized tracer response curves are summarized in Table 2. These data, in part, define the nature of the biopilot flow field. The extraction well data strongly suggests that the biopilot flow is not characterized by dead zones, periods of stagnation or short-circuiting. This is illustrated by the fact that the mean pore velocity variance at these three measuring points is less than 0.2 ft/day.

FIGURE 2
MEASURED (A) AND NORMALIZED (B) TRACER RESPONSE CURVES FOR BIOPILOT EXTRACTION WELLS



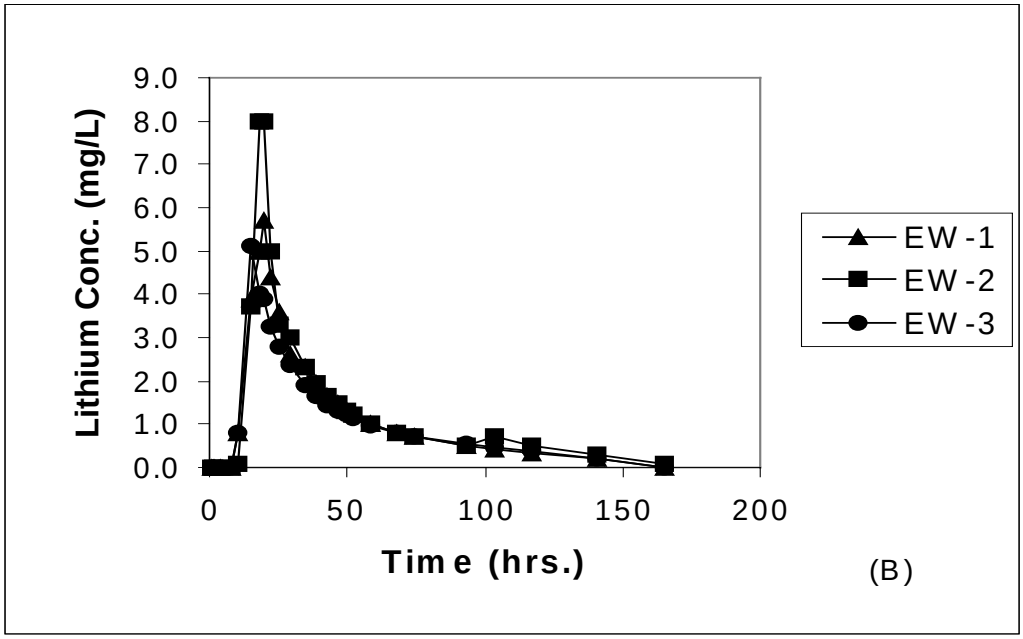


Table 2
Biopilot Flow Field Mean Pore Velocity Calculations

Well	Flow Path Length (ft)	Mean Residence Time[2] (hrs)	Mean Pore Velocity (ft/day)
EW-1	25.0	45.7	13.2
EW-2	25.0	48.3	12.5
EW-3	25.0	47.8	12.5
MW-1	12.7	58.0	5.3
MW-2	7.2	39.7	4.3
MW-3	17.9	42.4	10.0
SW-1	10.0	72.1	6.0
SW-2	17.6	70.3	3.4

The monitoring well data indicates that pore velocity decreases with depth. The calculated mean pore velocities at the bottom of the cell (i.e., 25 – 30 ft below ground surface) range from 3.4 ft/day at SW-2 to 10.0 ft/day at MW-3. The average value, 5.8 ft/day, is approximately one-half the average value (12.7 ft/day) calculated using the extraction well data alone. This finding shows that the water turnover rate in the upper region of the saturated zone (i.e., 15 - 25 feet below ground surface) must be considerably higher than the rate measured using the extraction well data.

The higher pore velocity for the upper region of the cell can be explained by higher conductivity. A decrease in flow along the bottom of the cell was expected due to boundary effects and changes in the soil matrix near the bottom of the cell. Sample borings taken early in the study indicated that clay stringers are present just above the cell bottom. Therefore, the variations measured in the flow field in the study are consistent with expectations based on stratigraphy.

6.4.2 Biopilot Hydrogeologic Properties

Porosity

Soil porosity is defined as total pore volume divided by the total volume. Effective porosity, defined as water occupied pore volume available for flow divided by total volume, is less than or equal to total porosity. Water table measurements before and after the tracer study showed that water depth did not change as the result of cell leakage or inflow. Consequently, effective porosity of the biopilot saturated zone matrix can be determined by examining tracer dilution.

Calculation of effective porosity by dilution is simplified because the total volume of the saturated zone is known to be 13,500 ft^3 from water table measurements. Given the mass of tracer added to the cell was 214,500 mg (i.e., 71,500 mg Li+ per well) and the equilibrium tracer concentration was 1.4 mg/L, the volume of water in the cell must equal 5,411 ft^3. This value divided by saturation zone volume (13,500 ft^3) equals 0.40, the effective porosity under the conditions of the test.

Another method of estimating effective porosity is to determine the pore volume occupied by displaceable water during passage of the tracer as discussed by Kaufman and Orlob (1956). Pore volume can be calculated from the expression:

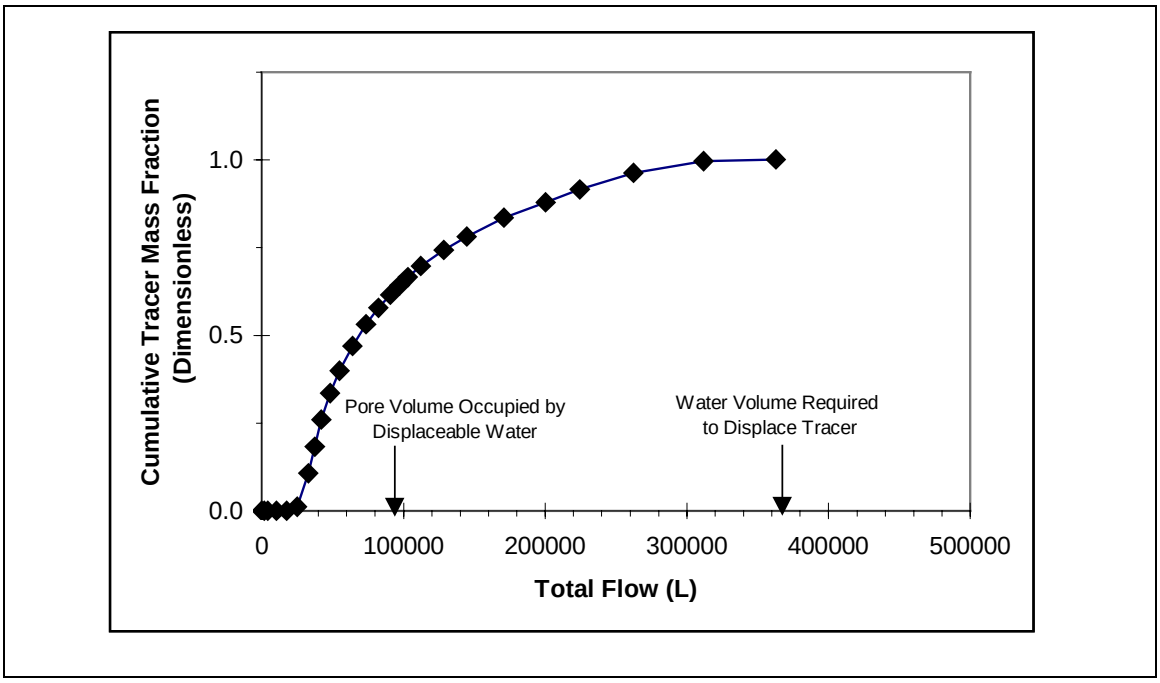
$$v_e = \int_0^V (1-c/c_o)dV$$

in which v_e is the pore volume, V is the volume of liquid necessary to displace the pore volume, c is the effluent tracer mass, and c_o is the total tracer mass.

Shown in Figure 3 is total flow versus cumulative tracer mass fraction for the extraction well monitoring points. Here, the cumulative mass fraction parameter is the average for the three wells. Pore volume may be evaluated by a graphical integration of the area above the tracer front. It is apparent that the total volume required to displace the tracer is

approximately 363,000 L. This volume minus the volume beneath the cumulative tracer mass fraction curve is equal to 96,300 L (3,400 ft^3). The effective porosity of the cell, then, is equal to 0.25, which is pore volume (3,400 ft^3) divided by the saturated volume of the cell (13,500 ft^3).

FIGURE 3
CUMULATIVE TRACER MASS FRACTION CURVE



Conductivity

Saturated hydraulic conductivity can be determined from Darcy's law which states:

$$q = -K(dh/dl)$$

where q = specific discharge, ft/day
K = conductivity, ft/day
h = head, ft
l = length, ft

The specific discharge, also known as Darcy's velocity, is the average pore velocity times the effective porosity. For this exercise, the gradient dh/dl was estimated by measuring the change in head between pairs of monitoring wells and dividing the difference by the distance between the wells. Because the recharge and extraction wells were closed by packers, water elevation readings at these positions could not be obtained. Water table measurements show that the gradient ranged from 0.02 ft/ft to 0.04 ft/ft. Because the water table slope probably increased close to the wells, the monitoring well measurements provide a low estimate of gradient.

Summarized in Table 3 are estimates of saturated horizontal conductivity based on the specific discharge data. Note that the conductivity estimates range from 125 and 250 ft/day for extraction well data. This range compares favorably with values reported by other investigators for the Upper Cohansey sand unit at TRS. For comparison, the horizontal saturated conductivity value used for modeling of cell flow during the design phase of the project was 113 ft/day.

TABLE 3
BIOPILOT SATURATED HYDRAULIC CONDUCTIVITY CALCULATIONS

Well	Specific Discharge (ft/day)	Gradient (ft/ft)	Hydraulic Conductivity (ft/day)
EW-1	5.0	0.02 – 0.04	125 – 252
EW-2	4.8	0.02 – 0.04	120 – 240
EW-3	4.8	0.02 – 0.04	120 – 240
MW-1	1.9	0.02 – 0.04	48 – 95
MW-2	1.7	0.02 – 0.04	43 – 85
MW-3	3.8	0.02 – 0.04	95 – 190
SW-1	2.4	0.02 – 0.04	60 – 120
SW-2	1.2	0.02 – 0.04	45 – 60

6.5 SUMMARY AND CONCLUSIONS

A study of the Ciba-Geigy biopilot saturated flow field was conducted using Li^+ as a non-reactive tracer. The tracer was added to the system as an impulse under normal operating

conditions. Tracer movement was monitored using samples from the extraction wells and monitoring wells and other components of the cell. After 165 hours, tracer concentration equilibrated at 1.4 mg/L and monitoring was discontinued.

Evaluation of the tracer response curves resulted in the following conclusions:

1. The biopilot saturated flow field is not characterized by dead zones, periods of stagnation or short-circuiting. The estimated mean pore velocity in the lower 10 feet of the cell (i.e., 20 – 30 ft below ground surface) is 12.7 ft/day.

2. The mean pore velocity decreases with depth to approximately 6 ft/day in the zone 25 – 30 ft below ground surface. Subsequently, the water turnover rate at the bottom of the biopilot is much less than in the upper part of the saturated zone.

3. Tracer dilution indicates that the effective porosity of the biopilot saturated zone may be as high as 0.40. An analysis of the pore volume occupied by displaceable water suggests the effective porosity may be as low as 0.25.

4. Estimates of the biopilot saturated horizontal hydraulic conductivity range from 120 – 240 ft/day.